National Contract for Lead Analysis Quality Assurance Project Plan

EPA has entered into a 5-year contract with RTI International to provide lead TSP filter analysis by Inductively-coupled Plasma Mass Spectrometry (ICP-MS) following EPA Federal Equivalent Method EQL-0510-191 and X-ray Fluorescence (XRF) analysis of PM10 filters following EPA Appendix Q to 40 CFR Part 50. RTI will only provide analysis results in accordance with the referenced methods and their Category 1 Quality Assurance Project Plan (QAPP).

EPA has approved their QAPP and all States purchasing analysis services under this contract agree to accept the procedures identified in the project plan.

Any questions/concerns regarding analysis services should be worked out between the State and RTI.

Analysis for Lead in TSP and PM10 Filters

Quality Assurance Project Plan

Prepared by
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Under Contract GS-23F-0147N

Prepared for
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OAR/OAQPS
U.S. Environmental Protection Agency

December 22, 2010

Approval Signatures

RTI Technical	Frank X. Weber	Date 12/22/10
RTI QA	Cynthia A. Salmons	Date 12/22/10
EPA Technical		Date 12/22/10
EPA QA		Date 12/23/10

Table of Contents

1.0 Project/Task Description

1.1 Background

RTI has been asked to provide analytical support for the U.S. Environmental Protection Agency's (EPA's) Office of Air Quality Planning and Standards (OAQPS) under contract GS-23F-0147N.

The objectives of this work are to provide TSP filter analysis by Inductively-coupled Plasma Mass Spectrometry (ICP-MS) following EPA Federal Equivalent Method EQL-0510-191 and X-ray Fluorescence (XRF) analysis of PM_{10} filters following EPA Appendix Q to 40 CFR Part 50. RTI will only provide analysis results in accordance with the referenced methods and this QAPP to the submitting agency(s). The methods are available at http://www.epa.gov and http://ecfr.gpoaccess.gov, respectively. This QAPP is a Category 1 as the data generated will be used to determine NAAQS attainment/non-attainment by the monitoring organizations submitting samples. Each organization submitting samples will have to formally accept the procedures in this QAPP and associated SOPs before analysis will be conducted.

Based on the EPA's review of the air quality criteria and national ambient air quality standards (NAAQS) for lead (Pb), revisions were made to the primary and secondary Pb NAAQS to provide requisite protection of public health and welfare, respectively. With regard to the primary standard, EPA revised the level to 0.15 μg Pb/m^3 in total suspended particles (Pb-TSP) and the averaging time to a rolling 3-month period with a maximum (not-to-be-exceeded) form, evaluated over a 3-year period. The secondary standard was revised by the EPA to be identical in all respects to the revised primary standard.

EPA revised the data handling procedures, including allowance for the use of Pb-PM_{10} data under certain circumstances, and ambient air monitoring and reporting requirements for Pb, including those related to sampling and analysis methods, network design, sampling schedule, and data reporting. EPA finalized a new FRM for Pb-PM_{10} monitoring based on the use of the already promulgated low-volume PM_{10C} FRM (40 CFR part 50, Appendix O) sampler coupled with XRF as the analysis method (Appendix Q).

1.2 RTI Personnel

Mr. Frank Weber is the RTI Project Manager (RTI PM) for this contract and will serve as the primary point of contact. E-mail is the preferred mode of contact and is shown in Table 1. As such, he is responsible for the quality of all services and deliverables. He will be assisted in that responsibility by Ms. Cynthia Salmons, the Quality Assurance (QA) Officer. Ms. Salmons will provide technical advice on quality issues, provide independent assessments of work processes and products, and manage the overall quality system for the work assignment. Ms. Salmons is independent of technical activities on the work assignment. Ms. Andrea McWilliams will lead the XRF testing and serve as a secondary point of contact. Mr. James Medlin will lead the ICP-MS analysis

work, with technical assistance from Mr. Frank Weber, and serve as a backup point of contact. Mr. Poitras will be the primary sample custodian and Mr. Burnette will serve as a backup.

Mr. Weber, Mr. Medlin, and Ms. McWilliams have all completed factory training on their respective instrumentation and each has more than nine years of experience with their respective analytical techniques. Each staff member has a training file detailing their experience, instrument qualifications, and documentation showing they have reviewed the QAPP and applicable SOPs.

1.3 QAPP Key Personnel

Table 1 lists the primary personnel and their affiliation to this QAPP.

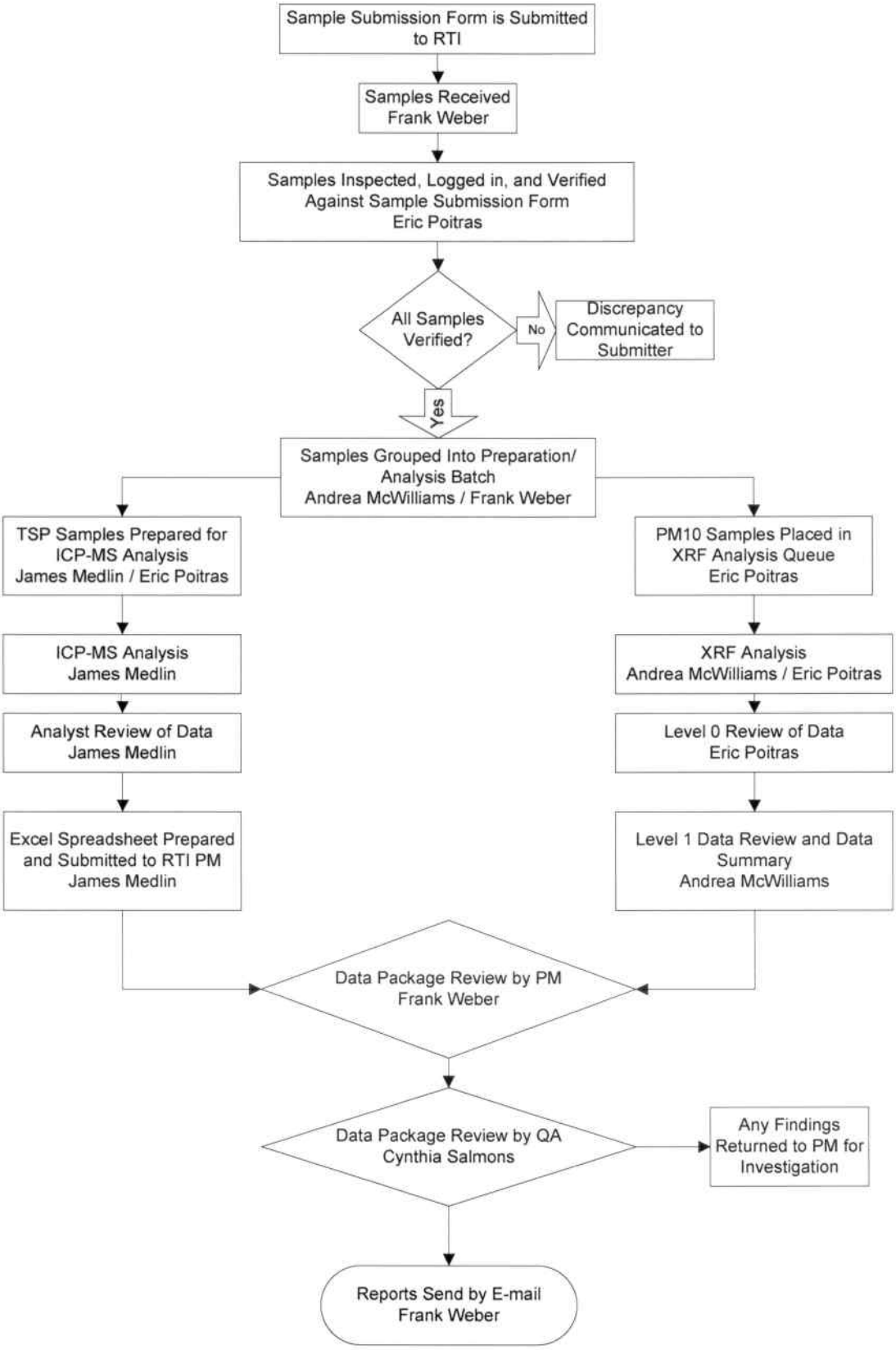
Table1. Key Personnel

Name	Affiliation	Function	Phone Number	E-mail
Frank Weber	RTI	RTI Project Manager	919-541-8762	fxw@rti.org
Andrea McWilliams	RTI	XRF Chemist	919-485-5520	acm@rti.org
James Medlin	RTI	ICP-MS Chemist	919-316-3445	jmedlin@rti.org
Cynthia Salmons	RTI	QA Officer	919-541-6948	cas@rti.org
Doug Burnette	RTI	Chemist	919-485-5560	tdb@rti.org
Eric Poitras	RTI	Chemist, Sample Custodian	919-316-3501	epoitras@rti.org
Margaret Dougherty	EPA	Contract Officer	919-541-2344	Dougherty.Margaret@epamail.epa.gov
Michael Papp	EPA	EPA QA Lead	919-541-2408	Papp.Michael@epamail.epa.gov
Joann Rice	EPA	Technical Expert	919-541-3372	Rice.Joann@epamail.epa.gov
Michelle Conner	RTI	TID Administration	919-541-6957	mconner@rti.org

1.4 Performance

The turnaround time on sample results will be 30 days from sample receipt. Results will be reported in Excel format. RTI will retain sample receipt records, chain of custody (COC) forms, extraction records for TSP filters, electronic copies of instrument data, and Excel final data reports. RTI will not maintain a master database of all results, only the Excel spreadsheets of final results. The TSP and PM10 filters will be retained for 6 months at which time the submitter may, at their cost, have the samples returned otherwise the filters will be disposed of. The sample flow path is shown in Figure 1.

Figure 1. Sample Flow Diagram



2.0 Analytical Methods

TSP Filters: EPA Designated Equivalent Method, EQL-0510-191, "Determination of Lead Concentration in TSP by ICP-MS with Heated Ultrasonic Nitric and Hydrochloric Acid Filter Extraction" for the analysis of Pb on TSP filters.

PM_{10} Filters: The FRM, Appendix Q to 40 CFR Part 50, "Reference Method for the Determination of Lead in Particulate Matter as PM_{10} Collected from Ambient Air", for the analysis of Pb on PM_{10} filters by XRF. The XRF instrument set up is accomplished per Section 6.2 of the XRF SOP. The method complies with all specifications and procedures in 40 CFR Part 50 Appendix Q for the analysis of Pb-PM_{10}. Only the analytical condition for Pb will be run and no weighing will be performed. The same XRF method used for $PM_{2.5}$ is used for PM_{10} analysis for Pb with no attenuation correction applied.

The methods are available on-line as shown in QAPP Section 1.1. Any edits or revisions to the FEM or FRM will be communicated to the submitting agencies by the PM through e-mail. Edits to the QAPP may arise from assessments, laboratory corrective actions, or review comments from submitting agencies. The PM will make edits and submit the QAPP to the RTI QA Officer for review, and then the QAPP will be submitted to a technical reviewer designated by the EPA Contact Officer. Once the revision is accepted by the EPA Contract Officer, a change notice and copy of the revised QAPP will be e-mailed to all submitting agencies.

3.0 Quality Control

The quality control objectives are strictly for the analysis of Pb in TSP and PM10 filters. If acceptance criteria listed in the SOPs and the QAPP are met the measurement data are considered valid for the objectives for which it was collected.

3.1 ICP-MS

Analytical quality control will follow the procedures outlined in the standard operating procedure. The specific quality control criteria for ICP-MS can be found in EQL-0510-191 (Appendix 1), Section 8. Section 8.8 addresses the analytical QC samples, Sections 8.2 through 8.7 and 8.9 address sample QC procedures. The calculation for sample results is shown in Section 12.2. The factor encompassing the strip size, dilution, and filter size is built into the experiment file and no post analysis processing is required.

Once results are generated the data is copied to a USB storage device and reviewed by the analyst, summarized in Excel format, and e-mailed to the PM who will review the data for correctness and completeness. This includes checking that all the QC specifications in Sections 8 and 9 of EQL-0510-191 are met. Once the PM has reviewed the Excel data file, it will be e-mailed to RTI QA for a final review. Once RTI QA completes a review of the file it will be returned to the PM for issuance to the submitter. The experiment file the data is collected in is the raw data and is backed up to an external hard drive at least quarterly. For

this project the experiment file will also be copied to dedicated USB storage device and all experiments for a month burned to compact disk. The CD will be labeled and sent to a fireproof safe located in the RTI archives at a site off main campus. This preserves the original data as collected in three separate locations.

3.2 XRF

The PM10 filters will only be analyzed for Pb. Only one instrument condition that has been optimized for Pb will be run. Specific quality control criteria for XRF can be found in Sections 10 and 11 of the attached SOP "Standard Operating Procedure for the X-Ray Fluorescence Analysis of Particulate Matter Deposits on Teflon Filters". All calculations are done by the instrument software, no post analysis processing of data is performed.

RTI will analyze NIST 2783 weekly. The recovery must be ±10% CV in order to be considered acceptable. A Micromatter thin film standard will be run with each tray of samples and the recovery must be ±5% CV.

Once results are generated the data is copied to a USB storage device and reviewed by the analyst, summarized in Excel format, and e-mailed to the PM who will review the data for correctness and completeness. The experimental data file is the raw data and is backed up to an external hard drive at least quarterly. For this project the experiment file will also be copied to a dedicated USB storage device and all experiments for a month burned to compact disk. The CD will be labeled and sent to a fireproof safe located in the RTI archives at a site off main campus. This preserves the original data as collected in three separate locations.

3.3 QA/QC Reports

RTI will compile the required quality control results for each batch of samples reported. The results will be reported with each batch of samples. The components of each analysis are summarized below:

TSP Filters by ICP-MS following EQL-0510-191:
Current MDL, Section 8.2
Reagent Blank and Reagent Blank Spike, Section 8.3
Duplicate sample and Spiked sample, Section 8.6
Serial Dilution, Section 8.7
Analytical QC summary, Section 8.8
CRM, Section 8.9
Calibration correlation coefficient and calibration standard recovery, Section 9.4

PM10 by XRF following Appendix 2:
Current MDL
Duplicate analysis of filters
Results for NIST 2783 (weekly)
Results for QC filter, FePb40c, (each tray)

MDLs will be performed on an annual basis or after any major repair or change to the instrument. ICP-MS triggers for redetermining MDLs would include the installation of a new detector, the replacement of the RF generator, or service that

involved the removal of the lens stack. XRF triggers would include the replacement of the power tube or detector.
All references to % recovery imply the standard formula of measured concentration divided by expected concentration times one hundred. Additionally, the formulas will be in the Excel data provided.

3.4 Data Quality Indicators

Typical data quality indicators such as method detection limits, duplicate samples, spiked samples, and quality control samples will be employed. A summary for each form of instrumentation is shown below.

ICP-MS

Precision:
The precision will be demonstrated by the analysis of duplicate sample preparations and serial dilutions. Acceptance criteria are shown in SOP Sections 8.6 and 8.7, respectively.
Bias:
The bias will be assessed for sample extractions by the analysis of spiked sample preparations, reagent blank spikes, and CRM preparations. Acceptance criteria are shown in SOP Sections 8.6 and 8.3, and 8.9, respectively. The analytical bias will be assessed through the analysis of ICV and CCV standards. Acceptance criteria are shown in SOP Section 8.8.
Detection Limits:
The method detection limit will be calculated per Section 8.2 of the SOP.
Completeness:
All sample and analytical recoveries must meet the acceptance criteria listed in the SOP. Any failures require the reanalysis of the samples or the repreparation of another strip from the filters. The RTI ICP-MS Data Review Checklist, Attachment 1, will document the review.

XRF

Precision:
The precision will be demonstrated by the duplicate analysis of samples. The precision must be 50 RPD when the lead level is $\geq$ 10X the uncertainty.
Bias:
The bias will be assessed by the analysis of NIST thin film standards. Acceptance criteria are shown in SOP Table 5.
Detection Limits:
The MDLs are calculated as three times the average counting uncertainty for each element. This is equivalent to a "3-sigma" MDL. The uncertainty calculation is defined in Section 9 of the XRF SOP.
Completeness:
All sample and QC criteria must be met in order to accept the data. Any failures will result in the reanalysis of the samples.

3.5 Assessments

Management and technical staff involved in any way with the contract will be fully committed to its execution as defined in the SOPs and the QAPP. All staff will be encouraged to provide recommendations for improvement of the process.

The PM will conduct an annual review of the program, preferably in the third quarter of the calendar year, and document any deficiencies and corrective action plans if required. The review will be summarized within two weeks and submitted to the RTI QA Officer for review and discussion. The RTI QA Officer will review any corrective action plans before implementation. Any deficiencies that could compromise data integrity will be reported to management and the EPA Contract Officer.

The RTI QA Officer will also conduct an annual review of the program, ideally in the first quarter of the calendar year, to document that the work is being performed according to the SOPs and QAPP and that all required documentation, records, and procedures are being performed. RTI SOPs ESE300 "Internal Quality Audits" and ESE 420 "Technical Assessments" will dictate the procedures for internal assessments. A summary report will be submitted to RTI management, the EPA Project Officer, and the PM within two weeks detailing the assessment. The summary report will include any deficiencies noted and corrective actions needed. The RTI QA Officer has the authority to stop project work in the event that deficiencies are found that could compromise data integrity. Management will acknowledge the receipt of the summary report by e-mail or memorandum.

RTI acknowledges that the EPA or their designee may, at their discretion, periodically conduct a site assessment of the program. The external assessment will be scheduled at a mutually convenient time to ensure that all key staff are available.

3.6 Discrepancy Reporting

All staff involved with the contract will be responsible for identifying nonconforming work and reporting it to the PM and QA Officer. The PM will investigate the root cause and document the issue and resolution in the project notebook. Analytical nonconformities will be investigated per RTI SOP TID-DAT-003, Procedures for Handling Aberrant and Out-of-Specification Data.

Any suspected discrepancies in reported data will be communicated to the PM via e-mail with the following information at a minimum:

- Requestor name and agency
- Date of nonconformity notice
- Sample ID(s)
- Suspected nonconformity, including specific details and rationale
- Date(s) of analysis

The PM will conduct a review of all data and records associated with the sample(s) and document the review in the project notebook. The review will be given to the RTI QA Officer for a secondary review. If an error is found it will be documented, the root cause determined, and a corrective action plan designed and

executed. If no error is found and the data is deemed correct RTI will, at the requestor's expense, perform a repeat extraction and analysis.

4.0 Instrument Calibration

The instrument calibration and verifications are detailed in the attached SOPs. Please refer to Section 9 in EQL-0510-191 (Appendix 1) and Section 6 in "Standard Operating Procedure for the X-Ray Fluorescence Analysis of Particulate Matter Deposits on Teflon Filters" (Appendix 2).

4.1 Instrument Inspection and Maintenance

The schedule of routine maintenance for the ICP-MS is shown in Table 2. The maintenance is documented in the instrument logbook. RTI has two X-Series ICP-MS units. Key spare consumable items kept on hand include: torch, nebulizer, spray chamber, cones, and pump tubing. The instruments are under service contract with the manufacturer and on site response is usually within two business days.

Prior to analysis each day, the instrument is tuned according to Section 9.2 and the instrument performance verified per Section 9.3. The performance check results are entered into the instrument logbook each day. The performance verification experiment file is backed up electronically each quarter.

If the instrument fails to meet the performance criteria as listed in Section 9.3, the laboratory manager (F. Weber) is contacted to review the instrument set-up and analysis. Any problems or calls for service are noted in the instrument logbook.

Table 2: X-Series II ICP-MS Routine Maintenance

Task	Daily	Weekly	Monthly	Quarterly	Yearly
Inspect cones, clean if necessary	x				
Inspect torch, clean if necessary	x				
Inspect spray chamber, clean if necessary	x				
Inspect nebulizer, clean if necessary	x				
Inspect pump tubing, replace if necessary	x				
Check chiller water level	x				
Check argon supply	x				
Check pump oil level		x			
Check air intake filters			x		
Check oil mist filter			x		
Change rotary pump oil				x	
Clean extraction lens *					x
Replace air filters *					x
Clean RF coil *					x
Inspect lens assembly *					x
Flush water chiller *					x

* These items are normally performed by a Thermo service technician during the annual preventive maintenance visit.

RTI has four XRF units and all are covered under service contract. The typical on-site response time is two business days. RTI keeps several key components on site for trouble shooting and repair: vacuum pump, E/I Board, 24v Power Supply, and a sample motor for the autosampler. The oil in the vacuum pump is changed once every three months or sooner if discoloration is noted in the sight window on the pump. The vacuum pump oil change is documented in the instrument logbook.

Prior to use each day an energy calibration is performed. If the energy line for copper shifts by more than 1eV the XRF laboratory manager is notified and the anomaly is documented in the instrument notebook. Any corrective action or calls for service are noted in the instrument logbook.

5.0 Sample Receipt and Custody

RTI will follow the attached SOP TID-LAB-005, "Metals and Inorganic Analysis Sample Receipt, Storage, and Tracking", to document the receipt and custody of the samples. Each sample will be given a unique RTI sample number upon receipt. The submitter sample ID and RTI sample ID will be entered into a spreadsheet that will be used to generate the final data report and a chain of custody (COC) form. The sample ID will be verified at each step of the extraction and analysis process.

Per contract GS-23F-0147N, Item 8, the submitting agency will be required to provide the listed information. RTI Sample Submission Form, Attachment 2, may be used to ensure all information is provided and expedite sample receipt. The samples must be shipped to:

RTI International
Attn: F. Weber, 6/207, GS-23F-0147N
3040 Cornwallis Road
Research Triangle Park, NC 27709

TSP filters must be in individual envelopes and PM10 filters must be in individual petri slides to prevent cross contamination. TSP and PM10 filters will be stored in the Building 6 Sample Custody Room (SCR) at ambient temperature in the shipping container the samples were received in or plastic containers with lids. All containers will be labeled with the project number and the date of receipt. Pb is not a volatile element and no refrigeration is required for sample storage. The RTI COC will be placed in a ziplock bag taped to the outside of the box or container.

Once analyzed, the ICP-MS extracts will be held for 6 months before disposal. The TSP filters will be held for 6 months; then the client may have them shipped back at their cost or authorize disposal. PM_{10} samples will be stored in their petri slide holders at ambient temperature for 6 months; then the client may have them shipped back at their cost or authorize disposal.

6.0 Consumables and Reagents

Stock standards and acids are commercially purchased and come with a certificate of analysis. The certificate of analysis is reviewed, initialed and dated by the analyst receiving the chemical, and placed into a binder. All chemicals are labeled with the chemical name, concentration, date received, expiration date, analyst initials, and storage conditions. Stock standards are verified by analysis against a second source (either calibrants or ICV). Reagents are tested per EQL-0510-191, Section 4.1 and documented in the project laboratory notebook.

Solutions prepared from commercial stock standards and reagent chemicals are labeled with the project number, solution name, concentration, date prepared, expiration date, analyst initials, and storage conditions. The preparation is documented in a laboratory notebook. Solutions prepared for the extraction and analysis of TSP filters by ICP-MS are shown in Table 3.

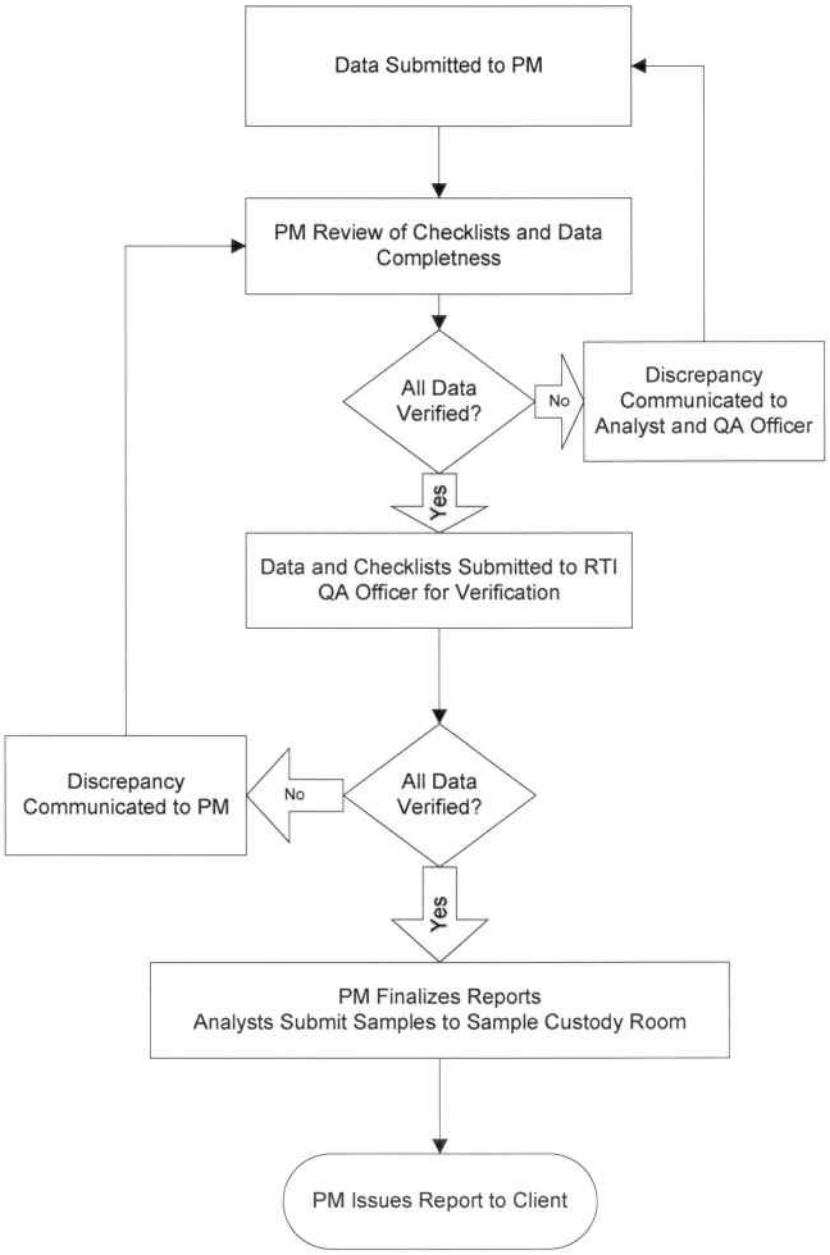
Table 3. Solution Preparation Frequency

Solution(s)	Frequency of Preparation
Extraction Solution	Weekly
Calibration Curve Standards	Monthly
Calibration Blank / ICB/ CCB	Monthly
ICV / CCV	Daily
LLCV	Daily

7.0 Data Review and Verification

Once data has been reviewed by the analyst, accepted by the RTI PM, and accepted by the QA Officer, the data will be submitted to the client in Excel spreadsheet format. Figure 2 shows the data flow path. The client will acknowledge receipt of the data by e-mail. In the event there are any questions regarding the data, the client will notify the RTI PM by e-mail per Section 3.6 of this QAPP.

Figure 2. Data Review



Attachment 1.

RTI ICP-MS Data Review Checklist

Parameter	Criteria	Analyst Initials
Correlation Coefficient	>0.998	
Calibration Standard Recovery	±10%	
ICV Recovery	±10%	
ICB Result	<Reporting Limit	
LLCV Recovery	±30%	
All CCV Recoveries	±10%	
All CCB Results	<Reporting Limit	
CCV/CCB Frequency	every 10 samples	
Reagent Blank (RB)	<Reporting Limit	
Reagent Blank Spike (RBS)	±20%	
CRM/NIST SRM Recovery	±20%	
Duplicate Sample Preparation	≤20 RPD	
Spiked Sample Preparation	±20%	
Serial Dilution Results	±10%	
Internal Standard Response	70 – 120%	
Data Summarized for Samples	Yes No	
Data Summarized for Sample QC	Yes No	
Data Summarized for Analytical QC	Yes No	

Analyst Review: _____ _____
Name Date

PM Review: _____ _____
Name Date

QA Review: _____ _____
Name Date

Attachment 2.

RTI TSP/PM10 Sample Submission Form

Date	Submitter	Submitter E-mail	Contract No.
			GS-23F-0147N

Quantity		Submitter Phone Number	Purchase Agreement No.
TSP	PM10	Notes:	

Number	Sample ID	RTI ID	Number	Sample ID	RTI ID
1			21		
2			22		
3			23		
4			24		
5			25		
6			26		
7			27		
8			28		
9			29		
10			30		
11			31		
12			32		
13			33		
14			34		
15			35		
16			36		
17			37		
18			38		
19			39		
20			40		

Appendices

Appendix 1 EQL-0510-191 Determination of Lead Concentration in TSP by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with Heated Ultrasonic Nitric and Hydrochloric Acid Filter Extraction

Appendix 2 Standard Operating Procedure for the X-Ray Fluorescence Analysis of Particulate Matter Deposits on Teflon Filters

Appendix 3 TID-DAT-003, Procedure for Handling Aberrant and Out-of-Specification Data.

Appendix 4 TID-LAB-005, Metals and Inorganics Analysis Sample Receipt, Storage, and Tracking.

Appendix 5 ESE 300, Internal Quality Audits

Appendix 6 EISD 420, Technical Assessments

Appendix 1

EQL-0510-191 Determination of Lead Concentration in TSP by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with Heated Ultrasonic Nitric and Hydrochloric Acid Filter Extraction, 22 pages

Determination of Lead in TSP by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with Heated Ultrasonic Nitric and Hydrochloric Acid Filter Extraction

Standard Operating Procedure (SOP)

Prepared by

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Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

DISCLAIMER

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Table of Contents

List of Figures

List of Tables

1.0 SCOPE AND APPLICABILITY

Lead poisoning can cause irreversible brain damage and can impair mental functioning in children. It can retard mental and physical development and reduce attention span. In adults, it can cause irritability, poor muscle coordination, and nerve damage to the sense organs and nerves controlling the body.

Since 1980, lead emissions have decreased nearly 97 percent, according to EPA, and levels of lead in the air are currently much lower than they were in 1978. The drop in emissions is being attributed primarily to the phase-out of lead in gasoline. However, EPA estimates that over 1,300 tons of lead are emitted into the air annually from sources including smelters, iron and steel foundries, and general aviation gasoline.[1] Based on its review of the air quality criteria and national ambient air quality standards (NAAQS) for lead (Pb), EPA has made revisions to the primary and secondary NAAQS for Pb to protect public health and welfare. EPA has revised the level to 0.15 $\mu g/m^3$ while it is retaining the current indicator of lead in total suspended particles (Pb-TSP).[2]

This Standard Operating Procedure (SOP) is for the Determination of Lead in TSP by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with Heated Ultrasonic Nitric and Hydrochloric Acid Filter Extraction.

NOTE: This SOP is based on USEPA's Office of Solid Waste (SW-846) Method 6020A – Inductively Coupled Plasma Mass Spectrometry.[3] Wording in certain sections of this SOP are paraphrased or taken directly from Method 6020A.

1.1 Inductively coupled plasma mass spectrometry (ICP-MS) is applicable for the sub-µg/mL determination of lead in a wide variety of matrices. This procedure describes a method for the acid extraction of lead in particulate matter collected on high-volume, glass fiber, TSP filters and measurement of the extracted lead using ICP-MS.

1.2 Due to variations in the isotopic abundance of lead, the value for total lead must be based on the sum of the signal intensities for isotopic masses, 206, 207, and 208. Most instrument software packages are able to sum the primary isotope signal intensities automatically.

1.3 ICP-MS requires the use of an internal standard. ^{115}In, ^{165}Ho, and ^{209}Bi are recommended internal standards for the determination of lead.

1.4 Use of this method is restricted to use by, or under supervision of, properly trained and experienced personnel. Requirements include training and experience

in inorganic sample preparation including acid extraction and also knowledge in the recognition and in the correction of spectral, chemical and physical interference in ICP-MS. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 This method describes the acid extraction of lead in particulate matter collected on 8 x 10 inch, glass fiber, ambient air filters using a high-volume TSP sampling device as described in 40 CFR Part 50, Appendix B[5] with subsequent measurement of the dissolved lead by ICP-MS. The Method Detection Limit (MDL) (sensitivity) was demonstrated to 0.0000161 µg/m^3 using Pb-spiked filter strips analyzed in accordance with the guidance provided in 40 CFR Part 136, Appendix B[6]. The method range was demonstrated from 0.00120 µg/m^3 to 0.480 µg/m^3, based on the low and high calibration curve standards and a nominal filter volume of 2000m^3.

2.2 This SOP includes one extraction method. In this method, a solution of nitric and hydrochloric acids is added to the filter samples in plastic tubes and the tubes are placed in a heated ultrasonic bath for one hour to facilitate the extraction of lead. Following ultrasonication, the samples are brought to a final volume of 40mL, vortex mixed or shaken vigorously, and centrifuged prior to aliquots being taken for ICP-MS analysis.

2.3 Calibration standards and check standards are prepared to matrix match the acid composition of the samples. ICP-MS analysis is then performed. With this method, the samples are first aspirated and the aerosol thus created is transported by a flow of argon gas into the plasma torch. The ions produced (e.g., Pb^{+1}) in the plasma are extracted via a differentially-pumped vacuum interface and are separated on the basis of their mass-to-charge ratio. The ions are quantified by a channel electron multiplier or a Faraday detector and the signal collected is processed by the instrument's software. Interferences must be assessed and corrected for, if present.

3.0 DEFINITIONS

Pb – Elemental or ionic lead

ICP-MS - Inductively Coupled Plasma Mass Spectrometer

MDL – Method detection limit

RL – Reporting limit

RSD – Relative standard deviation

RPD – Relative percent difference

ICB – Initial calibration blank

CCB – Continuing calibration blank

ICV - Initial calibration verification

CCV – Continuing calibration verification

LLCV – Lower Level Calibration Verification, serves as LLICV and LLCCV

RB - Reagent blank

RBS -Reagent blank spike

MSDS – Material Safety Data Sheet

NIST – National Institute of Standards and Technology

D.I. water - Deionized water

RTI – RTI International

SOP – Standard Operating Procedure

SRM – NIST Standard Reference Material

CRM – Certified Reference Material

USEPA – U.S. Environmental Protection Agency

v/v – volume to volume ratio

4.0 INTERFERENCES

4.1 Reagents, glassware, plasticware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. If reagent blanks, filter blanks, or quality control blanks yield results above the detection limit the source of contamination must be identified. All containers and reagents used in the processing of the samples must be checked for contamination prior to sample extraction and analysis. Reagents shall be diluted to match the final concentration of the extracts and analyzed for lead. Labware shall be rinsed with 0.38M HNO_3/0.84M HCl extraction solution and the solution analyzed. Once a reagent or labware article, such as extraction tubes, from a manufacturer have been successfully screened, additional screening is not required unless contamination is suspected.

4.2 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z) as the species of interest. There are no species found in ambient air that will result in isobaric interference with the three lead isotopes, 206, 207, and 208, being

measured. Polyatomic interferences occur when two or more elements combine to form an ion with the same mass-to-charge ratio as the isotope being measured. Lead is not subject to interference from common polyatomic ions and no correction is required.

4.3 The distribution of lead isotopes is not constant. The analysis of total lead should be based on the summation of signal intensities for the isotopic masses 206, 207, and 208. In most cases, the instrument software can perform the summation.

4.4 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers of the ICP-MS. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. These interferences are compensated for through use of internal standards. Sample dilution will reduce the effects of high levels of dissolved salts, but calibration standards must be prepared in the extraction medium and diluted accordingly.

5.0 HEALTH AND SAFETY CAUTIONS

5.1 This method does not address all the possible safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and compliance with all OSHA regulations. Material Safety Data Sheets (MSDS) for all chemicals used should be readily available to all personnel involved with the procedure.

5.2 Concentrated nitric and hydrochloric acids are moderately toxic and extremely irritating to the skin. Use these reagents in a hood, and if eye and skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection when working with these reagents. The component of this procedure requiring the greatest care is nitric acid (HNO_3). Nitric acid is a strong, corrosive, oxidizing agent that requires protection of the eyes, skin, and clothing. Items to be worn during use of this reagent include:

- Safety goggles (or safety glasses with side shields)
- Acid resistant rubber gloves
- A protective garment such as a laboratory apron. Nitric acid spilled on clothing will destroy the fabric and result in a hole; contact with the skin underneath will result in a burn.

It is also essential that an eye wash fountain or eye wash bottle be available during performance of this method. An eye wash bottle has a spout that covers the eye. If acid or any other corrosive gets into the eye, the water in this bottle is squirted onto the eye to wash out the harmful material. Eye washing should be performed with large amounts of water immediately after exposure. Medical help should be sought immediately after washing. If either acid, but especially nitric acid, is spilled onto the skin, wash immediately with large amounts of water. Medical attention is not required unless the burn appears to be significant. Even after washing and drying, the nitric acid may leave the skin slightly brown in color, this will heal and fade with time.

5.3 Lead (Pb) salts and lead solutions are toxic. Great care must be taken to ensure that samples and standards are handled properly; wash hands thoroughly after handling.

5.4 Care must be taken when using the ultrasonic bath as it is capable of causing mild burns. Chemists should refer to the safety guidance provided by the manufacturer of their specific equipment.

6.0 EQUIPMENT AND SUPPLIES

6.1 Apparatus

6.1.1 Thermo Scientific X-Series Inductively Coupled Plasma Mass Spectrometer (ICP-MS) or equivalent. The system must be capable of providing resolution better or equal to 1.0 amu at 10% peak height. The system must have a mass range from at least 7 to 240 AMU that allows for the application of the internal standard technique. For the measurement of lead, an instrument with a collision or reaction cell is not required.

6.1.2 Heated ultrasonic bath capable of maintaining a temperature of 80°C; VWR Model 750HT, 240W, or equivalent. Ultrasonic bath must meet the following performance criteria:

1. Cut a strip of aluminum foil almost the width of the tank and double the depth.
2. Lower the foil into the operating ultrasonic bath vertically until almost touching the bottom of the tank and hold for 10 seconds.
3. Remove the foil from the tank and observe the distribution of perforations and small pin prick holes. The indentations should be fine and evenly distributed. The even distribution of indentations indicates the ultrasonic bath is acceptable for use.

6.1.3 Laboratory centrifuge, Beckman GS-6, or equivalent.

6.1.4 Vortex mixer, VWR Signature Digital Vortex Mixer, VWR Catalog No. 14005-824, or equivalent.

6.2 Materials and Supplies

- Argon gas supply, 99.99% purity or better. National Welders Microbulk, or equivalent.
- Plastic digestion tubes with threaded caps for extraction and storage, SCP Science *Digi*TUBE® Item # 010-500-063, or equivalent.
- Pipette, Rainin EDP2, 100 µL, ± 1% accuracy, ≤1 %RSD (precision), with disposable tips, or equivalent.
- Pipette, Rainin EDP2, 1000 µL, ± 1% accuracy, ≤1 %RSD (precision), with disposable tips, or equivalent.
- Pipette, Rainin EDP2, 1-10 mL, ± 1% accuracy, ≤1 %RSD (precision), with disposable tips, or equivalent.
- Pipette, Thermo Lab Systems, 5 mL, ± 1% accuracy, ≤1 %RSD (precision), with disposable tips, or equivalent.
- Plastic tweezers; VWR Catalog No. 89026-420, or equivalent.
- Laboratory marker.
- Ceramic knife, Kyocera LK-25, or equivalent.
- Blank labels or labeling tape, VWR Catalog No. 36425-045, or equivalent.
- Graduated cylinder, 1 L, VWR 89000-260, or equivalent.
- Volumetric flask, Class A, 1 L, VWR Catalog No. 89025-778, or equivalent.
- Millipore Element deionized water system, or equivalent, capable of generating Type I water (>17.9 MΩ-cm).
- High purity glass fiber filters for use as blank filters for determination of MDL and laboratory blanks, Whatman EPM2000, or equivalent.

7.0 REAGENTS AND STANDARDS

7.1 Reagent- or trace metals-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications

of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

7.2 Concentrated nitric acid, 67-70%, SCP Science Catalog No. 250-037-177, or equivalent.

7.3 Concentrated hydrochloric acid, 33-36%, SCP Science Catalog No. 250-037-175, or equivalent.

7.4 Deionized water – All references to deionized water in the method refer to Type I deionized water with a resistivity >17.9 MΩ-cm.

7.5 Extraction solution (1.03M HNO_3 + 2.23M HCl). Prepare by adding 500mL of D.I. water to a 1000mL flask, adding 64.4mL of concentrated HNO_3 and 182mL of concentrated HCl, shaking to mix, allowing solution to cool, diluting to volume with reagent water, and inverting several times to mix. Extraction solution must be prepared at least weekly.

7.6 Standard stock solutions may be commercially purchased for each element or as a multi-element mix. Internal standards may be purchased as a mixed multi-element solution. The manufacturer's expiration date and storage conditions must be adhered to.

7.6.1 Lead standard, 1000 µg/mL, NIST traceable, commercially available with certificate of analysis. High Purity Standards Catalog No. 100028-1, or equivalent.

7.6.2 Indium standard, 1000 µg/mL, NIST traceable, commercially available with certificate of analysis. High Purity Standards Catalog No. 100024-1, or equivalent.

7.6.3 Bismuth standard, 1000 µg/mL, NIST traceable, commercially available with certificate of analysis. High Purity Standards Catalog No. 100006-1, or equivalent.

7.6.4 Holmium standard, 1000 µg/mL, NIST traceable, commercially available with certificate of analysis. High Purity Standards Catalog No. 100023-1, or equivalent.

7.6.5 Second source lead standard, 1000 µg/mL, NIST traceable, commercially available with certificate of analysis. Must be from a different vendor or lot than 7.6.1. Inorganic Ventures Catalog No. CGPB-1, or equivalent.

7.6.6 Standard Reference Materials, NIST SRM 2583[7], 2586[8], 2587[9] or 1648[10], or equivalent.

Note: The In, Bi, and Ho internal standards may also be purchased as 10 µg/mL standards Calibration standards are prepared by diluting stock standards to the appropriate levels in the same acid concentrations as in the final sample volume (0.38M HNO_3 + 0.84M HCl). The typical range for calibration standards is 0.005 to 2.00 µg/mL. At a minimum the curve must contain a blank and five (5) lead containing calibration standards. The calibration standards shall be stored at ambient laboratory temperature. Calibration standards must be prepared weekly and verified against a freshly prepared ICV using a NIST-traceable source different from the calibration standards.

7.7 Internal standards may be added to the test solution or by on-line addition. The nominal concentration for an internal standard is 0.010 µg/mL (10 ppb). Bismuth is the preferred internal standard for lead but holmium and indium may be used in the event the sample contains bismuth and high recoveries are observed.

7.8 Three laboratory blank solutions are required for analysis: (1) the calibration blank is used in the construction of the calibration curve and as a periodic check of system cleanliness (ICB and CCB); (2) the reagent blank (RB) is carried through the extraction process to assess possible contamination; and (3) the rinse blank is run between samples to clean the sample introduction system. If reagent blanks or laboratory blanks yield results above the detection limit, the source of contamination must be identified. Screening of labware and reagents is addressed in Section 4.1.

7.8.1 The calibration blank is prepared in the same acid matrix as the calibration standards (0.38M HNO_3 + 0.84M HCl) and samples and contains all internal standards used in the analysis.

7.8.2 The Reagent Blank (RB) contains all reagents used in the extraction and is carried through the extraction procedure at the same time as the samples.

7.8.3 The rinse blank is a solution of 1-2% nitric acid (v/v) in reagent grade water. A sufficient volume should be prepared to flush the system between all standards and samples analyzed.

7.8.4 EPA procures filters and distributes them to the state monitoring agencies collecting Pb in support of the National Ambient Air Quality Standard (NAAQS). If filter lot blanks are provided to the laboratory for analysis, consult 40CFR, Appendix G to Part 50, Section 6.1.1 for guidance on testing.

7.9 The Initial Calibration Verification (ICV), Lower Level Calibration Verification (LLCV), and Continuing Calibration Verification (CCV) solutions are prepared from a different lead source than the calibration curve standards and at a concentration that is either at or below the midpoint on the calibration curve, but within the calibration range. Both are prepared in the same acid matrix as the calibration standards. Note that the same solution may be used for both the ICV and CCV. The ICV/CCV and LLCV solutions must be prepared fresh daily.

7.10 Tuning Solution. Prepare a tuning solution according to the instrument manufacturer's recommendations. This solution will be used to verify the mass calibration and resolution of the instrument.

8.0 QUALITY CONTROL

8.1 Standard quality control practices shall be employed to assess the validity of the data generated. Included are: Method Detection Limit (MDL), Reporting Limit (RL), Reagent Blank (RB), duplicate samples, spiked samples, serial dilutions, ICV, CCV, LLCV, ICB, CCB, and SRMs/CRMs.

8.2 MDLs must be calculated by analyzing seven replicates of a known low-level spike added to a filter strip and carried through the entire extraction procedure. The test solutions shall be spiked at 2-5 times the estimated MDL. The MDL is defined as 3.143 times the standard deviation of the seven replicates in accordance with 40 CFR Part 136, appendix B[6]. The reporting limit, RL, is defined as the lowest calibration standard included in the curve or the LLCV concentration. Results reported below this limit must clearly be marked as estimated. See Method 6020A, Section 10.4.3 for additional guidance.

8.3 For each batch of samples, one method or reagent blank (RB) and one method or reagent blank spike (RBS) spiked at the same level as the sample spike (see 8.6) must be prepared and carried throughout the entire process. The results of the RB must be below the RL. The recovery for the RBS must be within ± 20% of the expected value. If the reagent blank yields a result above the RL, the source of contamination must be identified and the extraction and analysis repeated. Reagents and labware must be suspected as sources of contamination. Screening of reagents and labware is addressed in Section 4.1.

8.4 Any samples that exceed the highest calibration standard must be diluted and rerun so that the concentration falls within the curve. The minimum dilution will be 1 to 5 with a 0.38M HNO_3 and 0.84M HCl solution.

8.5 The internal standard response must be monitored during the analysis. If the internal standard response falls below 70% or rises above 120% of expected due

to possible matrix effects, the sample must be diluted and reanalyzed. The minimum dilution will be 1 to 5 with a 0.38M HNO_3 and 0.84M HCl solution. If the first dilution does not correct the problem, additional dilutions must be run until the internal standard falls within the specified range.

8.6 For every batch of samples prepared, there must be one duplicate and one spike sample prepared. The spike added is to be at a level that falls within the calibration curve, normally the midpoint of the curve. The initial plus duplicate sample must yield an RPD of ≤ 20. The spike must be within ± 20% of the expected value.

8.7 For each batch of samples, one extract must be diluted five fold and analyzed. The corrected dilution result must be within ±10% of the undiluted result. The sample chosen for the serial dilution shall have a concentration at or above 10X the lowest standard in the curve to ensure the diluted value falls within the curve. If the serial dilution fails, chemical or physical interference should be suspected.

8.8 ICB, ICV, LLCV, CCB and CCV samples are to be run as shown in the following table.

Sample	**Frequency**	**Performance Specification**
ICB	Prior to first sample	Below the RL
ICV	Prior to first sample	Within 90 to 110% of the expected value
LLCV	Daily, before first sample and after last sample	±30% of the expected value
CCB	After every 10 extracted samples	Less than the RL
CCV	After every 10 extracted samples	Within 90-110% of the expected value

If any of these QC samples fails to meet specifications, the source of the unacceptable performance must be determined, the problem corrected, and any samples not bracketed by passing QC samples must be reanalyzed.

8.9 For each batch of samples, one certified reference material (CRM) must be combined with a blank filter strip and carried through the entire extraction procedure. A blank filter strip spiked with a NIST traceable solution different from that used for preparing the calibration standards or a solid CRM combined with a blank filter strip in the extraction tube are acceptable for use. The result must be within ±20% of the expected value.

8.10 For each run, a LLCV must be analyzed. The LLCV shall be prepared at a concentration not more than three times the lowest calibration standard and at a concentration not used in the calibration curve. The LLCV is used to assess performance at the low end of the curve. If the LLCV fails the run must be terminated, the problem corrected, the instrument recalibrated, and the analysis repeated.

8.11 Pipettes used for volumetric transfer must have the calibration checked at least once every 6 months and pass ± 1% accuracy and ≤1 %RSD (precision) based on five replicate readings. The pipettes must be checked weekly for accuracy with a single replicate. Any pipette that does not meet ± 1% accuracy on the weekly check must be removed from service, repaired, and pass a full calibration check before use.

9.0 CALIBRATION

Follow the instrument manufacturer's instructions for the routine maintenance, cleaning, and ignition procedures for the specific instrument being used.

9.1 Ignite the plasma and wait for at least one half hour for the instrument to warm up before beginning any pre-analysis steps.

9.2 For the Thermo X-Series with Xt cones, aspirate a 10 ng/mL tune solution containing In, Bi, and Ce. Monitor the intensities of In, Bi, CE, and CeO and adjust the instrument settings to achieve the highest In and Bi counts while minimizing the CeO/Ce oxide ratio. For other instruments, follow the manufacturer's recommended practice. Tune to meet the instrument manufacturer's specifications. After tuning, place the sample aspiration probe into a 2% nitric acid rinse solution for at least 5 minutes to flush the system.

9.3 Aspirate a 5 ng/mL solution containing Co, In, and Bi to perform a daily instrument stability check. Run 10 replicates of the solution. The %RSD for the replicates must be less than 3% at all masses. If the %RSD is greater than 3%, the sample introduction system, pump tubing, and tune should be examined, and the analysis repeated. Place the sample aspiration probe into a 2% nitric acid rinse solution for at least 5 minutes to flush the system.

9.4 Load the calibration standards in the autosampler and analyze using the same method parameters that will be used to analyze samples. The curve must include one blank and at least 5 lead-containing calibration standards. The correlation coefficient must be at least 0.998 for the curve to be accepted. The lowest standard must recover ± 15% of the expected value and the remaining standards must recover ± 10% of the expected value to be accepted.

9.5 Immediately after the calibration curve is completed, analyze an ICV and an ICB. The ICV must be prepared from a different source of lead than the calibration standards. The ICV must recover 90-110 % of the expected value for the run to continue. The ICB must be less than the RL. If either the ICV or the ICB fails, the run must be terminated, the problem identified and corrected, and the analysis re-started.

9.6 A LLCV, CCV and a CCB must be run after the ICV and ICB. A CCV and CCB must be run at a frequency of not less than every 10 extracted samples. The CCV solution is prepared from a different source than the calibration standards and may be the same as the ICV solution. The LLCV must be within ± 30% of expected value. The CCV value must be within ± 10% of expected for the run to continue. The CCB must be less than the RL. If either the CCV, LLCV, or CCB fails, the run must be terminated, the problem identified and corrected, and the analysis re-started from the last passing CCV/LLCV/CCB set.

9.7 A LLCV, CCV, and CCB set must be run at the end of the analysis. The LLCV must be within ± 30% of expected value. If either the CCV, LLCV, or CCB fails, the run must be terminated, the problem identified and corrected, and the analysis re-started from the last passing CCV/LLCV/CCB set.

10.0 FILTER STRIP EXTRACTION

All plasticware (e.g., Nalgene) and glassware used in the extraction procedures is soaked in 1% HNO_3 for at least 24 hours and rinsed with reagent water prior to use. All mechanical pipettes used must be calibrated to ±1% accuracy and ≤ 1% RSD at a minimum of once every 6 months.

10.1 Sample Preparation – Heated Ultrasonic Bath

10.1.1 Using a ceramic knife and non-metal ruler, cut a 3/4 in. X 8 in. strip from the exposed area of the filter by cutting a strip from the edge of the filter where it has been folded along the 10” side at least 1 in. from the right or left side to avoid the un-sampled area covered by the filter holder. The filters must be carefully handled to avoid dislodging deposits.

10.1.2 Using plastic tweezers, roll the filter strip up in a coil like a cinnamon bun and place the rolled strip in the bottom of a labeled 50mL extraction tube (See Figure 1). In a fume hood, add 15.0 ± 0.15 mL of the extraction solution (Section 7.5) using a calibrated mechanical pipette. Ensure that the extraction solution completely covers the filter strip.

10.1.3 Loosely cap the 50mL extraction tube and place it upright in a plastic rack (See Figure 2). When all samples have been prepared, place the racks in an uncovered heated ultrasonic water bath that has been preheated to 80 ± 5°C and ensure that the water level in the ultrasonic is above the level of the extraction solution in the tubes but well below the level of the extraction tube caps to avoid contamination. Start the ultrasonic bath and allow the unit to run for 1 hour ± 5 minutes at 80 ± 5°C.

10.1.4 Remove the rack(s) from the ultrasonic bath and allow the racks to cool.

10.1.5 Add 25.0 ± 0.25 mL of D.I. water with a calibrated mechanical pipette to bring the sample to a final volume of 40.0 ± 0.4 mL. Tightly cap the tubes and vortex mix or shake vigorously. Place the extraction tubes in an appropriate holder and centrifuge for 20 minutes at 2500RPM.

CAUTION- Make sure that the centrifuge holder has a flat bottom to support the flat bottomed extraction tubes.

10.1.6 Pour an aliquot of the solution into an autosampler vial for ICP-MS analysis to avoid the potential for contamination. Do not pipette an aliquot of solution into the autosampler vial.

10.1.7 Decant the extract to a clean tube, cap tightly, and store the sample extract at ambient laboratory temperature. Extracts may be stored for up to six months from the date of extraction.

11.0 MEASUREMENT PROCEDURE

11.1 Follow the instrument manufacturer's startup procedures for the ICP-MS.

11.2 Set instrument parameters to the appropriate operating conditions as presented in the instrument manufacturer's operating manual and allow the instrument to warm up for at least 30 minutes.

11.3 Calibrate the instrument per Section 9 of this SOP.

11.4 Verify the instrument is suitable for analysis as defined in Sections 9.2 and 9.3.

11.5 As directed in Section 8 of this SOP, analyze an ICV and ICB immediately after the calibration curve followed by a LLCV, then CCV and CCB. The acceptance requirements for these parameters are presented in Section 8.8.

11.6 Analyze a CCV and a CCB after every 10 extracted samples.

11.7 Analyze a LLCV, CCV and CCB at the end of the analysis.

11.8 Typical run samples will include field samples, field sample duplicates, spiked field sample extracts, serially diluted samples, the set of QC samples listed in 8.8 above, and one or more CRMs/SRMs.

11.9 Any samples that exceed the highest standard in the calibration curve must be diluted and reanalyzed so that the diluted concentration falls within the calibration curve.

12.0 RESULTS

12.1 The filter results must be reported in µg/mL as analyzed. Any additional dilutions done must be accounted for in the instrument software. The internal standard recoveries must be included in the result calculation; this is done by the ICP-MS software for most all commercial instruments. Final results should be reported in µg Pb/m^3 to three decimal places as follows in 12.2.

12.2 $$C = \frac{(\mu g\ Pb/mL\ X\ 40mL/strip\ X\ A)}{V_s}$$

Where:

C = Concentration, µg Pb / m^3

µg Pb/mL = Lead concentration in solution

40.0 mL/strip = Total extraction solution volume

A = Area correction = 63.0in^2 sampled / 5.25in^2 analyzed = 12.0

V_s = Actual volume of air sampled

The calculation assumes the use of a standard 8" X 10" TSP filter which has a sampled area of 9" X 7" (63.0in^2) due to the ½" filter holder border around the outer edge. The ¾" X 8" strip has a sampled area of ¾" X 7" (5.25in^2). If filter lot

blanks are provided for analysis, refer to 40CFR, Appendix G to Part 50, Section 6.1.1 for guidance on testing.

13.0 METHOD PERFORMANCE

Information in this section is an example of typical performance results achieved by following this SOP. Actual performance must be demonstrated by each individual laboratory and instrument.

13.1 Performance data has been collected to determine the method detection limit (MDL) for this method. MDLs were determined for the ultrasonic/ nitric and hydrochloric acid extraction method in accordance with 40 CFR Part 136, Appendix B[6]. Table 1 shows the MDLs determined from seven reagent/filter blank solutions and seven reagent/filter blank solutions spiked with low level lead at three times the estimated MDL. The MDLs are well below the USEPA requirement of 5% of the current Pb NAAQS or 0.0075 $\mu g/m^3$.

13.2 Recovery tests with filter strips spiked with NIST SRMs were performed using the ultrasonic/ nitric and hydrochloric acid filter extraction method and measurement of the dissolved lead with ICP-MS. Table 2 shows recoveries with these standard reference materials. The recoveries for the SRMs are $\geq$ 90% at the 95% confidence level.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. The sources of pollution generated with this procedure are waste acid extracts and lead-containing solutions.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St. N.W., Washington, D.C., 20036, www.acs.org.

15.0 WASTE MANAGEMENT

15.1 Laboratory waste management practices must be conducted consistent with all applicable rules and regulations. Laboratories are urged to protect air, water, and land by minimizing all releases from hood and bench operations, complying with

the letter and spirit of any sewer and discharge permits and regulations, and by complying with all solid and hazardous waste regulation. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society listed in Section 14.2.

15.2 Waste nitric acid, hydrochloric acid, and solutions containing these reagents and/or Pb must be placed in labeled bottles and delivered to a commercial firm that specializes in removal of hazardous waste.

16.0 REFERENCES

[1] (http://www.thompson.com/public/index.jsp) Last accessed 09/08/09.

[2] 40 CFR Parts 50, 51, 53, and 58, National Ambient Air Quality Standards for Lead; Final Rule.

[3] Method 6020A – Inductively Coupled Plasma Mass Spectrometry. U.S. Environmental Protection Agency. Revision 1, February 2007

[4] 40 CFR, Part 50, Appendix G - Reference Method for the Determination of Lead in Suspended Particulate Matter Collected From Ambient Air.

[5] 40 CFR**,** Part 50, Appendix B — Reference Method for the Determination of Suspended Particulate Matter in the Atmosphere (High-Volume Method)

[6] 40 CFR**,** Part 136, Appendix B — Definition and Procedure for the Determination of the Method Detection Limit – Revision 1.1

[7] NIST, *Certificate of Analysis: Standard Reference Materials 2583,Trace Elements in Indoor Dust, Nominal 90 mg/kg Lead*, National Institute of Standards and Technology, Gaithersburg, MD, 1998.

[8] NIST, *Certificate of Analysis: Standard Reference Materials 2586, Trace Elements in Soil. Nominal 500 mg/Kg Lead*, National Institute of Standards and Technology, Gaithersburg, MD, 2008.

[9] NIST, *Certificate of Analysis: Standard Reference Materials 2587, Trace Elements in Soil Containing Lead from Paint, Nominal 3000 mg/Kg Lead*, National Institute of Standards and Technology, Gaithersburg, MD, 2008.

[10] NIST, *Certificate of Analysis: Standard Reference Materials 1648, Urban Particulate Matter, 0.655±0.033% Lead*, National Institute of Standards and Technology, Gaithersburg, MD, 2008.

17.0 FIGURES AND TABLES

Figure 1. Top view of filter strip rolled and placed in 28mm diameter plastic extraction tube.

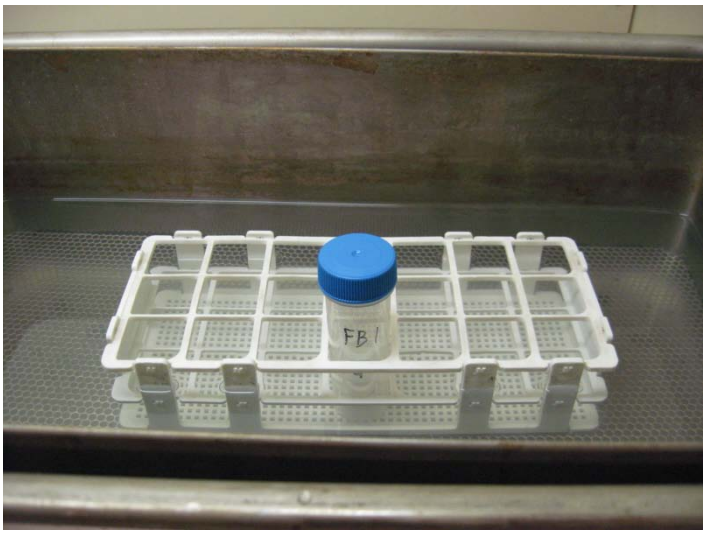

Figure 2. Filter in plastic extraction tube in tube rack placed in ultrasonic bath.

Table 1 . Method Detection Limits Determined by Analysis of Reagent/Glass Fiber Filter Blanks and Reagent/Glass Fiber Filter Blanks Spiked with Low-level Pb Solution.

Ultrasonic Extraction Method	Blank (µg/m^3)*	Pb-spiked (µg/m^3)*
n=1	0.0000434	0.0000702
n=2	0.0000420	0.0000715
n=3	0.0000439	0.0000611
n=4	0.0000407	0.0000587
n=5	0.0000437	0.0000608
n=6	0.0000437	0.0000607
n=7	0.0000403	0.0000616
Average	0.0000425	0.0000635
Standard Deviation	0.0000015	0.0000051
MDL**	0.0000047	0.0000161

* Assumes 2000 m^3 air sample.

** MDL is 3.143 times the standard deviation of the results for seven consecutive sample replicates analyzed.

Table 2. Recoveries of Lead from NIST SRMs Spiked onto TSP Glass Fiber Filters.

Extraction Method	**Recovery, ICP-MS, (%)**		
	NIST 2586 Soil	**NIST 2587 Soil**	**NIST 1648 Dust**
Ultrasonic Bath	89.8±1.7	96.8±5.3	93.2±3.6

Appendix 2

Standard Operating Procedure for the X-Ray Fluorescence Analysis of Particulate Matter Deposits on Teflon Filters, 17 pages

Standard Operating Procedure for the X-Ray Fluorescence Analysis of Particulate Matter Deposits on Teflon Filters

Environmental and Industrial Measurements Division
RTI International*
Research Triangle Park, North Carolina

Prepared by: _____ Date: 12/21/10

Reviewed by: _____ Date: 12/21/10

Approved by: _____ Date: 12/21/10

RTI INTERNATIONAL

* RTI International is a trade name of Research Triangle Institute.

Contents

Standard Operating Procedure for the X-ray Fluorescence Analysis of PM Deposits on Teflon Filters

1.0 Scope and Application

This standard operating procedure addresses the application of energy dispersive X-ray fluorescence (EDXRF) spectrometry to the determination of trace elements in particulate matter (PM) deposits on Teflon filters. This technique is capable of quantitative analysis of elements with atomic numbers 11 (sodium) through 92 (uranium). The 33 elements specific to this project are listed in Table 1.

Table 1. Project-Specific Elements Analyzed for the PM Speciation Program

Element	Element	Element	Element
Sodium (Na)	Titanium (Ti)	Arsenic (As)	Indium (In)
Magnesium (Mg)	Vanadium (V)	Selenium (Se)	Antimony (Sb)
Aluminum (Al)	Chromium (Cr)	Bromine (Br)	Cesium (Cs)
Silicon (Si)	Manganese (Mn)	Rubidium (Rb)	Barium (Ba)
Phosphorus (P)	Iron (Fe)	Strontium (Sr)	Cerium (Ce)
Sulfur (S)	Cobalt (Co)	Zirconium (Zr)	Lead (Pb)
Chlorine (Cl)	Nickel (Ni)	Silver (Ag)	
Potassium (K)	Copper (Cu)	Cadmium (Cd)	
Calcium (Ca)	Zinc (Zn)	Tin (Sn)	

1.1 Principle

The basis of X-ray fluorescence (XRF) spectrometry is the interaction of X-ray photons from a separate excitation source with atoms of the elements of interest found in the sample (filter deposit). When these excitation photons interact with the atoms in the sample, the photons cause the ejection of inner shell electrons. Outer shell electrons then fall into these vacancies. These transitions result in the emission of X-rays that are characteristic of the element. The energy of the characteristic X-ray is equal to the difference in the electron-binding energies of the two electron shells involved in the transition. Because the electron-binding energies are a function of the atomic number, the energy of the X-ray is characteristic of the element. The number or intensity of X-rays produced at a given energy provides a measure of the amount of the element present by comparisons with standards.

The X-rays are detected with a semiconductor material, lithium-drifted silicon. The X-ray passing into the detector produces a pulse of electrical current; the more energetic the X-ray, the larger the pulse of electrical current. The electrical pulses are measured and counted with appropriate electronics. These analyzer electronics further process the signals and display the X-ray energy spectrum (numbers of X-rays versus energy) on a personal computer (PC). The computer software determines the energy and intensity of the characteristic X-ray peaks, and then calculates the elemental concentrations through comparison to calibration parameters. The analysis of PM filter deposits is based on the assumption that the thickness of the deposit is small with respect to the analyte characteristic X-ray transmission thickness. It is assumed that the overall production of fluorescence X-rays is equivalent for PM samples and thin film, elemental standards. Therefore, the concentration of analytes in an unknown sample is determined by first calibrating the spectrometer with thin-film standards to determine sensitivity factors, and then analyzing the unknown samples under identical excitation conditions as used to determine the calibration factors.

1.2 Method Overview

The first step is to check the energy calibration to ensure that peak energies are accurately tied to specific elements. Energy adjustment is performed using a ThermoNoran copper (Cu) calibration standard. This procedure is run every day before any analysis is performed. The energy adjustment involves measuring the Cu Kα line (8041), and then determining the difference between the measured peak energy value and the ideal value and if any adjustments are required, the instrument software performs it automatically.

Filter samples are removed from cold storage and are loaded into the sample cups. Sample information is entered into the instrument logbook. The filters (in their sample cups) are loaded into the XRF sample tray in the same order as they are written into the instrument logbook. The instrument is then prepared for analysis by entering each filter aliquot number into the Method Tray List within the WinTrace software. The PM filter deposit analysis is then initiated.

This analysis protocol consists of each filter being analyzed five separate times using five different excitation conditions (See Section 6.2, *Method Setup*). The specific excitation conditions have been optimized for specific groups of elements listed in Table 1. The different excitation conditions are used to maximize the sensitivity of the measurement of the different groups of elements, which fluoresce over a wide range of excitation energies. Each analytical run, which includes nine samples, has a multi-element thin film standard to verify overall method and instrumentation performance.

Quantitative calibration for the elements is based on the use of thin film, elemental standards available from Micromatter, Inc. Recalibration of the instrument is required when the quality control samples or the National Institute of Standards and Technology standard falls outside their acceptance limits, when the detector or tube is replaced, or when the instrument undergoes significant repair or other changes in the hardware. Typical recalibration frequency is on the order of once every 6 to 12 months.

2.0 Safety

Operating the ThermoNoran QuanX XRF analyzer under normal operations and following Good Laboratory Practices to provide a safe working environment, but the following cautions should be noted.

ThermoNoran QuanX XRF analyzer operators are protected from accidental exposure to X-rays by a lid lock and front and back door interlocks when the instrument is in operation. Monthly the RTI Radiation Safety Officer performs area monitoring around each instrument to check for any leaking radiation. Also, the operator wears one to monitor his or her exposure. If any problems arise with the "X-RAYS ON" indicator light on the sample chamber lid or the interlock system, contact the instrument service engineer.

A beryllium (Be) window is present to separate the sample chamber from the X-ray tube and detector. Because this window is fragile and brittle, do not allow sample or debris to fall onto the window and avoid using compressed air to clean the window because it will cause the window to rupture. If the window should rupture, it is important to note that Be metal is poisonous. Use extreme caution when collecting pieces of Be and consult the instrument service engineer for advice on cleaning up the broken window and replacing it.

3.0 Filter Sample Considerations

It is assumed that the PM material is uniformly deposited on the filter and that the position of the PM filter and the standards in the instrument is the same. It is important that care be taken when loading filters into the sample cups so that the deposit is not scraped, smudged, or smeared in any way. Care also needs to be taken to assure that the filters are placed flat in the sample cups and that these cups rest flat on the instrument sample-positioning wheel.

4.0 Interferences and Intensity Corrections

The following sections describe potential sources of error in the procedure:

4.1 Spectral Interferences

Spectral interferences with analyte line intensity determination include elemental peak overlap, escape peak, and sum peak interferences. These interferences are automatically corrected within the method program. No action is required by the XRF operator once these interferences have been addressed within the method.

4.2 Background Correction

The laboratory background correction is determined using 10 blank, unused Teflon filters. These filters are analyzed on the XRF instrument for the 33 elements. Only those elements for which the average laboratory blanks values is above three times the uncertainty calculated by ThermoNoran software are subjected to background correction. A median value is determined for each of the select elements with a background above three times the uncertainty, and this median value is subtracted from the measured value for each of these elements to make the corrections. The correction values are entered into the software for automatic correction of field sample data.

4.3 Particle Size Effects

The X-ray production efficiency is affected by particle size for the lightest elements, such as aluminum; however, PM particle size effects are substantially less than 1 percent for most elements. Because the true particle size distribution cannot be determined for any given filter without microscopic analysis of that filter, no correction for particle size is performed.

4.4 Attenuation Correction

X-ray attenuation occurs when incoming (excitation) x-ray photons are absorbed by the sample before causing the desired fluorescence and when outgoing (fluorescent) photons are absorbed by the sample before escaping the sample. The net effect is that the instrument detects less signal from an element than would be expected if there is no attenuation correction; smaller values indicate a greater attenuation effect. RTI Attenuation correction software accounts for the excitation energies used in the RTI ThermoNoran QuanX XRF instruments. The software, which is a modification of a routine used by EPA, determines attenuations and their uncertainties for both thin, homogeneous deposits principally from aerosol condensation and also from deposits that contain particles with diameters in the high end of the $PM_{2.5}$ size range. The software is applied to RTI's XRF data post measurement to correct for the attenuation before that data is posted in the AQS.

5.0 Instruments

Three ThermoNoran QuanX XRF analyzers (i.e., bench top, laboratory grade, EDXRF spectrometers) are used for this procedure. Each instrument uses a high flux rhodium anode X-ray tube, which is positioned to direct excitation X-rays through one of five preselected filters onto the sample. Standard equipment for each instrument includes an electronically cooled lithium-drifted silicon (Si[Li]) solid-state X-ray detector, a 10-position sample filter wheel, and pulse-processing electronics that communicate spectral data to a PC, which displays and processes spectral information and outputs elemental concentration data. Each analyzer contains the following major components:

- ThermoNoran QuanX cabinet that contains the detector, X-ray tube, and sample changer and electronics for system control and signal processing.
- PC with the ThermoNoran WinTrace software.

- Vacuum pump.
- Printer for analysis reports.
- Uninterruptible power supply, which supplies the instrument, PC, and the vacuum pump with 6 hours of uninterruptible power.

6.0 Instrument Calibration

6.1 Standards

Standards used for calibration consist of single or two non-interfering elements deposited as thin film standards from Micromatter, Inc; the standards are prepared by vacuum deposition resulting in highly uniform deposits. The 31 Micromatter standards used for calibration at RTI are listed in Table 2.

Table 2. Micromatter Calibration Standards

Analyte	Analyte	Analyte	Analyte
Sodium or chlorine as NaCl	Titanium as Ti metal	Zinc as ZnTe	Indium as In metal
Magnesium as Mg metal	Vanadium as V metal	Arsenic as GaAs	Tin as Sn metal
Aluminum as Al metal	Chromium as Cr metal	Selenium as Se metal	Antimony as Sb metal
Silicon as SiO	Manganese as Mn metal	Bromine or cesium as CsBr	Cesium as CsF_2
Phosphorus or gallium as GaP	Iron as Fe metal	Rubidium as RbI	Barium as Ba F_2
Sulfur as CuSx	Cobalt as Co metal	Strontium as Sr F_2	Cerium as CeF_3
Potassium as KI	Nickel as Ni metal	Silver or mercury as Ag-Hg Amalgam	Lead as Pb metal
Calcium as Ca F_2	Copper as Cu metal	Cadmium or selenium as CdSe	

6.2 Method Setup

The standardization procedure consists of following steps:

- Set up reference peak spectra: Acquisition of reference spectra is required when performing calibration. As long as no processing methods have changed, these peak shape references remain valid. The procedure of acquiring reference spectra consists of analyzing thin film standards or pure element material (as listed in Table 2) and acquiring individual elemental spectra that are stored in the Method File with each of the analytical conditions. The reference spectra must be interference free, and the peak count for the reference spectra must be greater than 30,000 counts. These reference spectra are used in

the standard deconvolution and mathematical separation of overlapping peaks of the unknown spectra.

- Select acquisition conditions and analysis technique: Five different excitation conditions are performed during the analysis, as shown in Table 3. The specific excitation conditions have been optimized for specific groups of elements listed in Table 1. The different excitation conditions are used to maximize the sensitivity of the measurement of the different groups of elements, which fluoresce over a wide range of energies. When creating the excitation conditions, there are two operational parameters that are typically used and need to be considered (as shown in Table 4). These are determination of live time and atmospheric conditions, which will depend on the elements of concern and the detection limits that need to be achieved. Typically, for the lighter the elements, the live time is set to 300, and the atmospheric condition is set to vacuum.

Table 3. Excitation Conditions

Condition		Filter	Atmospheric Conditions	Voltage (kV)	Current (mA)	Analytes*
1	Low Za	None	Vacuum	4	1.98	Na and Mg
2	Low Zb	Graphite	Vacuum	10	1.98	Al, Si, P, S Cl, K, and Ca
3	Mid Za	Pd thin	Vacuum	30	1.66	Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cs, Ba, and Ce
4	Mid Zc	Pd thick	Vacuum	50	1.00	As, Se, Br, Rb, Sr, and Pb
5	High Za	Cu thin	Vacuum	50	1.00	Zr, Ag, Cd, In, Sn, and Sb

Cs, Ba, Ce, Pb, are quantified from L-lines; all other elements are quantified from the K-lines.

Table 4. Operational Parameters

Parameter	Description
Live time	This is pre-set in the Method File; for the unknown samples, each excitation condition is set to between 200 and 300 seconds live time
Atmosphere	This is pre-set in the Method File; for the unknown samples, each excitation condition will operate under vacuum

- Set up standards file: The Micromatter standards listed in Table 2 are manually entered into a Standards Library and imported into the Method File. The information provided in the Standards Library is the standard name, identification number, and certified concentration of the particular standard. The software will not allow the measurement of the standards until the standard file is imported into the Method File.

- Measurement of standards: After the Standards Library is imported into the Method File, the analyst proceeds with calibration by clicking the calibrate icon. The software will prompt to acquire all spectra for the standards. Verify that the standards are placed in the sample tray correctly, then start the acquisition. The software will acquire all the necessary spectra to perform the calibration. Because the method is quantifying for 33 elements and the sample tray is for 10 samples, the software will prompt for the next tray to be loaded after finishing the first 10 standards.
- Determine background correction: Laboratory background correction is determined using 10 blank, unused Teflon filters. These filters are analyzed for the 33 elements. Only the elements for which the average laboratory blank value is above three times the uncertainty calculated by ThermoNoran software are subjected to background correction. A median value is determined for the select elements with background levels above three times the uncertainty, and this median value is subtracted from the measured value for each of these elements to make the correction. The correction is manually added into the software under the Coefficients view, for automatic correction of the data.
- Validate calibration: After the standards and reference spectra have been acquired and the background correction has been applied, the round-robin samples (See Section 12 regarding the round-robin program) and the NIST 1832, along with Micromatter standards (as unknowns) are analyzed to verify calibration and check recoveries for each element of concern. A typical adjustment to the calibration is due to the +/- 5% error with the Micromatter standards. If an element's recovery is too high or low when the standard has been analyzed as an unknown, then an adjustment is made within the Coefficients view of the Method File to accurately correct for the error with the standard.
- Run unknowns: After the instrument has successfully performed calibration, quantitative analysis can be performed on real-world samples.

6.3 Calibration Frequency

Calibration is performed only when the quality assurance/quality control (QA/QC) limits are exceeded or if there is a change in the excitation and/or detection conditions, such as a change in the tube, detector, X-ray filters, or signal processor. Calibrations are typically valid for 6 months to 1 year.

7.0 Filter Handling

Teflon filters are received from RTI's Gravimetric Laboratory after being weighed to determine the mass (loading) of the filter. Custody of the Teflon filters is transferred to RTI's XRF Laboratory by signing the appropriate chain-of-custody forms. The filters are placed in cold storage (refrigerator in Building 6) until they are scheduled for analysis. Note that the filters are analyzed at room temperature and under vacuum conditions.

8.0 Filter Preparation and Analysis

8.1 Preparation

Filters scheduled for analysis are removed from cold storage and are allowed to come to room temperature. With a 10-tray autosampler, the QA standard will always be loaded into position 10, and the unknowns will start out with position 1 and will continue to position 9. The analyst will wear powder-free gloves when working with the filters and samples holders. Before any filters are loaded into the sample cups, the cups must be wiped with a Kimwipe to remove any residue left behind from the previous filters. This will eliminate potential cross-contamination. To load a filter into a sample cup, first remove the top of the Petri slide. Next, turn over the Petri slide into the sample cup with the exposed area of the filter now face down in the cup and ready for analysis. The filter will gently fall from the Petri slide into the cup. If a filter is stuck in the Petri slide, cleaned forceps are used to gently grab the filter by the outer ring and to place it face down into the sample cup. Place the sample cup in the next available tray position and write down the filter aliquot number in the instrument's logbook. Recording the tray position and filter aliquot number in the logbook will allow the operator to cross check the information when entering the filter information into the WinTrace software for analysis. No other preparation of the samples is required.

8.2 Analysis

After the filters are loaded into the sample cups and loaded into the sample tray, a Method Tray List is created in Acquisition Manager within the WinTrace software. The Method Tray List will allow for automated quantitative analysis in conjunction with a Method File. The Method Tray List is created by entering the first sample identification and choosing the Method File from the directory. After the Method File is opened by Acquisition Manager and the sample position is verified in the tray as being correct, then proceed to enter the next sample on the next line. The program automatically fills in the Method File specified for the previous sample.

After the Method Tray List is set up, click the spectrum icon on the toolbar to start the acquisition. The chamber lid will latch and the "X-RAYS ON" warning light will illuminate and the vacuum pump will click on. After a 300-second warm up, acquisition will begin starting with the lowest power condition.

9.0 Data Acquisition and Calculations

After all the spectra have all been acquired (they are saved in the respective Method File), Method Explorer will process the spectrums and display the analytical results in a specific format. The instrumental analysis report details the analyte, concentration, uncertainty, peak counts per second (cps), and background cps.

To obtain the analytical results of the unknowns, go into Method Explorer and open the respective Method File. Under sample lists, identify the samples needed, and then click on the analysis report item to obtain the results in an rtf format. Save the report onto the hard drive. The

results file must be converted from the rtf format to a csv format to be able to upload to the RTI XRF database. ThermoNoran provided RTI with an external program to complete the conversion. After the data has been converted, it is an acceptable format to upload into the RTI XRF database for report generation, uncertainty determinations, attenuation correction through EPA provided software, and perform QC analysis. During report generation, the unit concentration $\mu g/cm^2$ is multiplied by the sample area, 11.86 cm^2, to obtain the value for μg/filter.

The WinTrace XRF software does not calculate uncertainty values when the peak and concentration result is zero (i.e., peak area $\leq$ background area). To obtain the uncertainty values for when the result is zero, a calculation is performed during the import into the RTI XRF database. The calculation is

$$\text{Uncertainty} = \text{Slope} * A * \text{sqrt}\,(3 * \text{sqrt}\,(B * t) + B * t)/t$$

Where:

Slope is the response slope calculated in the method

B = Background count rate (cps)

A = Scaling factor for converting to $\mu g/cm^2$

t = Live time

10.0 Quality Control

Several different QC activities are performed as part of the analysis procedure. These activities, their frequency, the measures of acceptable performance, and action if the item fails performance standards are provided in Table 5.

Table 5. Quality Control Procedures

Item	Inspection Frequency	Inspection Parameter	Action If Item Fails Inspection	Documentation Required
Energy calibration	Daily	Wavelength alignment of the instrument	This is an automated process	Document in the instrument's run logbook
Calibration verification	Monthly	Percentage of recovery of seven elements on thin-film National Institutes of Standards and Technology reference materials	Adjust instrument calibration factors	Document in the instrument's run logbook; results stored in the XRF database
	Monthly	90% to 110% recovery analyzing the PM2.5 calibration standards as unknowns		Results stored in instrument's method file
Ongoing calibration verification	Run with every tray of samples	90% to 110% recovery using a multi-element sample containing Ti, Fe, Cd, Se, Pb, and SiO deposits of 5-10µg/cm^2	Re-check instrument calibration and adjust if necessary; re-analyze samples	Document in the instrument's run log book
Background Determination	Monthly	Analysis of 10 blank, unused Teflon filters. All elements below three times the uncertainty	Adjust instrument background values	Documented in instruments run logbook

11.0 Data Review and Validation

The analytical dataset undergoes Level 0 and Level 1 validations. These levels of validation will ensure that the dataset being reported will be of good quality.

11.1 Level 0 Validation

A Level 0 validation begins with the analyst, who identifies any problems related to the chain-of-custody, the filter, or any mechanical or software problems that might have occurred during the analysis of the filters. If such items are identified, the analyst notes any problems in the instrument logbook, which is reviewed by the Technical Area Supervisor.

11.2 Level 1 Validation

A Level 1 validation is a more technical review of the analytical data. This review starts with the analyst, but it will primarily be performed by the Technical Area Supervisor. Using the review

criteria developed by the QA Manager, the responsibilities of the analyst and the Technical Area Supervisor are provided in Table 6.

If any discrepancies are noted by the analyst or the Technical Area Supervisor, they will be reported on their respective checklist (Figure 1 and Figure 2).

Table 6. Level 1 Validation Responsibilities

Analyst	Technical Area Supervisor
Verify proper custody documentation is provided in batch folder	Ensure analytical dataset is complete and the proper procedures were followed to analyze the filters
Check sample identifications against COC forms and proper number of samples match given COC	Check that proper paperwork is provided in the batch folder and for any notations regarding the analysis of the batch or flaws with the filters that were analyzed
Confirm mass values for each sample are present on final report	Review precision, accuracy, and replicate data for acceptable limits
Make sure sample identifications are consistent between final report versus pre-attenuation report	Check data for any inconsistencies or trends and report to QA Manager
Review pre and post attenuation reports for disparity with attenuated data	Apply flags to data , if applicable

After two levels of review have been performed on the analytical dataset, it is ready to be submitted for upload into the CSN database.

Batch Creation Date:_____ Batch ID Number:_____

Number of Samples:_____

(circle one, if no leave comment why)

Item #1: Custody Documentation

Chain-of-Custody form present Yes No

Signed By:_____

Dated:_____

Sample Identification

No. of samples matches number on COC form Yes No

ID#s on COC match Id #s on samples Yes No

Item #2: Attenuation Correction

Sample IDs consistent with pre-attenuation report Yes No

Mass values present on report Yes No

Item #3: Data Comparison Pre-attenuation vs Attenuated Data

Results consistent between pre and post attenuation Yes No

Comments Regarding Data:_____

_____

_____

_____

Reviewer Signature:_____ Date Signed:_____

Figure 1. EDXRF Analysis Analyst Checklist.

COC Form No. _____ Report Date: _____

Data Review:

Sample Filter No. _____ Comments: _____

Sample Filter No. _____ Comments: _____

Sample Filter No. _____ Comments: _____

Sample Filter No. _____ Comments: _____

Sample Filter No. _____ Comments: _____

Sample Filter No. _____ Comments: _____

Quality Control Review:

Precision Data Acceptable? Yes ____ No ____ Notes: _____

Accuracy Data Acceptable? Yes ____ No ____ Notes: _____

Replicate Data Acceptable? Yes ____ No ____ Notes: _____

Chain-of-Custody Data Cover Letter Yes ____ No ____ Notes: _____

Filter-Loading Masses: Yes ____ No ____ Notes: _____

Reviewed by: _____ _____
Date

Figure 2. EDXRF Analysis Technical Area Supervisor Checklist.

12.0 XRF Round-Robin Comparison Program

The XRF Round-Robin Filter Exchange Program is intended to provide an ongoing comparison of analysis results generated by the two laboratories that analyze XRF samples for the Chemical Speciation Network (CSN) Program. Exposed (real-world) filters obtained from the CSN archive are used to provide the most realistic samples possible. According to the contract with EPA, filters and aliquots must be kept for 5 years in case the state monitoring agencies want to re-analyze them or have them returned to the respective agency.

12.1 Selection of Filters

To find filters that are likely to yield the most useful data, the database is periodically searched for filter samples that have the following characteristics:

- Represents a range of different elements at levels above the analytical uncertainties (queries have been designed to select filter sets that maximize the number of different measurable elements)
- Represents a range of different concentrations, from low to high (but above the uncertainty levels)
- No data validity flags or codes
- In good condition by visual inspection.

12.2 Distribution of Filters, Data Tracking, and Reporting

The selected filters in their Petri slides are in the CSN archive based on their box numbers, which can be obtained from the CSN database. Filters are already in Petri slides and are marked by their original aliquot numbers (assigned when the filter was received from the field). Filters are visually inspected before further processing, and any defective filters are not used as round robins. Filters are assigned a new aliquot number and are transferred into new Petri slides labeled with new barcode stickers. This is conducted to make the sample partially blind to the laboratories when they are re-analyzed; however, filters are identified as round-robin samples so that laboratories operating two or more XRF instruments for the CSN Program can analyze them on all of their instruments before sending them back to RTI.

The aliquot number is linked in the database to measurement request ID number R28598T. Using a special measurement request ID allows data to be easily retrieved after the round-robin filters have been analyzed.

The filters are incorporated into normal shipments to the participating XRF laboratories, including RTI. On average, at least two round-robin filters per month are analyzed by each laboratory. Laboratories with multiple XRF instruments analyze the round-robin filters on each instrument

Each round-robin filter should be analyzed at least once by every participating laboratory (and instrument). Analysis of the same filter multiple times by the same laboratory is not considered to

be a problem; however, filters are rotated out of use after approximately 6 months of use and are replaced by new round-robin filters selected as described in Section 12.1 above.

Data are reported back from the participating XRF laboratories, including RTI, along with all the regular data. The round-robin data are uploaded into the CSN database, along with all the regular data. Round-robin results are ignored by the data-processing routines used for validating and reporting routine and blank filter data. The round-robin data are accessible in the CSN database using the unique measurement request number assigned to the Round-Robin Program.

Database queries have been developed that extract the round-robin XRF data, as well as the original values reported for the filter, and report them in a tabular format suitable for importing into Microsoft Excel or another data management and analysis tool.

12.3 Interpretation of Results and Corrective Actions

The most effective means of interpreting the results has been found to be plots of individual round-robin results versus the median of results for all reporting laboratories and instruments. The original result is usually included in the dataset from which the median is determined.

Systematic problems are defined as particular element/laboratory/instrument combinations that are consistently above the median by a significant amount. This amount is assessed relative to the uncertainty values that are reported along with the concentration data. Identification of problems is similar to the technique used with control charts: a potential problem would be indicated under the following conditions, where "1-sigma" is the uncertainty value for the element reported by the laboratory:

- One sample beyond 3-sigma.
- Two samples beyond 2-sigma (both in the same direction).
- Five samples beyond 1-sigma (all in the same direction).

Whenever an element or a set of elements appears to be systematically high or low relative to the median results as previously described, the laboratory with the bias (same procedures for all participating XRF laboratories, including RTI) is contacted and is asked to recalibrate the instrument and/or to review its QC data for the time period during which the questioned round-robin samples were analyzed. If the laboratory identifies a problem that requires recalibration, it will recalculate all data for the affected elements during the questioned time period and will resubmit the data to RTI, where it will be uploaded into the CSN database, replacing the previous data.

Appendix 3

TID-DAT-003

Procedure for Handling Aberrant and Out-of-Specification Data, 7 pages

AUTHORED BY: Signed _____
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Date 9/22/04

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Elizabeth A. Hill, EISD Manager
Date 9/23/04

INITIAL EFFECTIVE DATE: October 1, 2004

See last page of SOP for Review and Revision history.

Table of Contents

1.0 PURPOSE

This procedure describes the process for handling aberrant and out-of-specification (OOS) data.

2.0 SCOPE

A Standard Operating Procedure (SOP) or written work plan (protocol, validation plan) is followed for each specific analysis. There are, however, instances where deviations in the analytical results occur when the analytical procedure, instrumentation, reagents, or test sample itself produces an out-of-control analytical condition such that the result (aberrant data) is not representative of the test sample. Deviations may also occur when the analytical measurement is otherwise in control but the result does not meet client expectations or specifications for the test sample under evaluation. Data of this variety are referred to as out-of-specification (OOS) results. The following document provides procedures for investigating and documenting the source of either type of the deviation as well as determining whether retesting is appropriate

3.0 RESPONSIBILITY

3.1 Management

The laboratory supervisor is responsible for reviewing remedial actions taken to eliminate the cause of aberrant data. The laboratory supervisor is also responsible for giving written approval of remedial actions taken by the analyst to replace aberrant data. Supervisor approval may be documented by (1) a signature authorization in the research laboratory notebook (or benchsheet) or (2) a memorandum to the file (for a more extensive explanation of the deviation and corrective action).

For OOS results, the supervisor is responsible for informing the client of the results and for leading an investigation of the events or circumstances which may have led to OOS results.

3.2 Quality Assurance (QA) Officer

The QA Officer (QA/QC) is responsible for performing a review or audit of all documentation including standard operating procedures, the research laboratory notebook or benchsheet, and draft report(s) to ensure that the documentation accurately reflects the work performed and meets the requirements for GLP/cGMP compliance.

The QA review results in preparation of an audit report which delineates findings on non-compliance as well as provides suggestions for improved compliance in future work. The analyst must provide responses to the findings in the audit; these findings must be approved by the laboratory supervisor. The QA Officer then adds to the QA audit report to indicate that all findings have been appropriately addressed and that the data and analytical report have undergone a review by the QA Officer. For OOS results, the QA Officer reviews the written result of the investigation and the justification for retesting, if performed.

3.3 Personnel

The analyst is responsible for documenting (1) that Standard Operating Procedures (SOPs) or other appropriate documents were followed for every analysis or (2) that deviations in the analytical procedures were employed. In the latter case, it is the responsibility of the analyst to obtain approval from the supervisor for such deviations, where possible. Where unexpected results are encountered, the analyst is responsible for documenting the cause of the aberrant data if an instrumental or procedural problem is identified, or alerting laboratory management if an OOS result is suspected. The analyst is responsible for clearly documenting, within the research laboratory notebook or benchsheet, all actions taken to remediate the cause of the aberrant data or to investigate the source of the OOS results. This documentation must be reviewed and approved by the laboratory supervisor before any report including the analytical data is prepared. This can be accomplished by the laboratory supervisor signing the notebook page or benchsheet where the explanation is recorded.

4.0 PROCEDURE

Failure of analytical data to meet expectations or specifications requires the laboratory supervisor and the analyst to perform an investigation to determine the cause and thus whether the failure is aberrant data or an OOS result.

4.1 Initial Investigation

As soon as the data problem is noted, a preliminary investigation is performed by the analyst to identify any out-of-control analytical conditions and includes the following:

(1) Verification of sample identity (correct sample and/or lot)

(2) Verification that the testing procedure was current

(3) Verification of analytical system performance (e.g., system suitability, system and reagent blanks, calibration controls)

(4) Evaluation of the raw data (e.g., fits the test sample).

If an incorrect sample identity or an analytical system performance error is clearly identified, the datum is classified as an aberrant result. For an aberrant result, a re-analysis (retest) of the sample is performed if the supervisor confirms the analyst's conclusion. The error, its cause, and the step(s) taken to eliminate the problem for re-analysis must be fully documented in the research laboratory notebook or benchsheet and approved by the laboratory supervisor. The new analytical result replaces the previous aberrant data result; averaging of in-specification data and aberrant data are not allowed.

If an out-of-control condition is not found, the data is considered an OOS result. The client will then be notified, and a formal investigation shall be performed with the client's approval.

4.2 Formal Investigation

A formal investigation is conducted if an initial investigation fails to determine whether the cause of the unexpected result is from an out-of-control analytical condition, and is therefore considered an OOS result. The formal investigation includes the following:

(1) The laboratory supervisor discusses the results of the initial investigation with the Project Manager (if different) and the QA Officer

(2) The laboratory supervisor or project manager discusses the OOS data and the results of the initial investigation with the client

(3) The laboratory supervisor develops a specific plan for re-analysis of the test sample based upon (1) and (2) and obtains QA Officer review and client approval

(4) The analyst performs the specified re-analysis.

Both sets of data are reported to the client.

A written report of the initial investigation and formal investigation of the OOS results must be completed within 20 business days of the failure. This report includes a description of the investigative steps taken, raw data involved, findings, and conclusions. The OOS report becomes a permanent part

of the sample analysis record after review and approval by the Project Manager and review by the QA Officer.

REVIEW & REVISION HISTORY

Version	Describe Major Changes or Indicate "Reviewed with No Revisions"	Effective Date/ Review Date	New Review Date
0	New SOP ; Replaces SOP 795-003	09/15/2004	09/2006
1	Revised to remove replacement information this SOP does not replace SOP 795-003.	10/01/2004	10/2006
1	Reviewed; no revision required.	10/01/2004	10/2008
1	SOP has been reviewed, no revision required.	10/01/2004 5/15/2007	5/2009
1	SOP has been reviewed, no revision required.	10/01/2004 3/4/2009	3/4/2012

Instructions:

- For revisions, authors increment the version number and add the description of change to this form. Upon receipt of the signed, revised SOP, the SOP Coordinator assigns the new effective date.
- For reviews with no revisions, the SOP Coordinator updates this page and assigns the next date for review upon receipt of a completed review notice.

Appendix 4

TID-LAB-005

Metals and Inorganics Analysis Sample Receipt, Storage, and Tracking, 10 pages.

AUTHORED BY:	Signed	Michael A. Levine, Research Chemist
	Date	4/28/05
QA REVIEWED BY:	Signed	Celia D. Keller Celia D. Keller, Asst. QA Manager
	Date	04/28/05
APPROVED BY:	Signed	Elizabeth A. Hill Elizabeth A. Hill, Sr. Director, EISD
	Date	05/02/05

INITIAL EFFECTIVE DATE: MAY - 3 2005

See last page of SOP for Review and Revision history.

Table of Contents

1.0 PURPOSE

This document describes a procedure for sample receipt, storage, and tracking.

2.0 SCOPE

This SOP applies to all regulated and non regulated projects within the Trace Inorganics Department (TID) except for those which have established project-specific protocols or SOPs for sample receipt, storage and tracking.

3.0 RESPONSIBILITY

All Trace Inorganic Department (TID) staff members who receive, store, or track samples for analytical studies should follow the procedures described in this document, unless other procedures apply as described above.

4.0 PROCEDURE

4.1 Materials Needed

1) Sample receipt notebook – This is a permanently bound, sequentially numbered RTI notebook.
2) Sample Receipt Form (See Attachment 1: for example) – This form (or a form containing similar information) is used when receiving the sample(s). All fields are filled out as appropriate. This form is securely affixed in a sample receipt notebook.
3) Sample Custody and Tracking form (See Attachment 2: for example) – This form is to be used to track the location of samples as they are processed. This form is securely affixed in a sample receipt notebook.
4) Combined Sample Receipt, Custody and Tracking Form (See Attachment 3: for example) - For studies of limited sample batch size, the sample receipt, custody, and tracking activities may more conveniently be recorded on one combined form.

4.2 Sample Receipt and Login

1) The Project Leader or Department Manager assigns a sample custodian to a set of samples. This person will be responsible for the receipt, tracking, and storage of the incoming samples. If the sample custodian is unavailable when samples arrive, another staff member may act as temporary custodian for the purpose of receiving and logging in the samples.

The temporary custodian will fill out the appropriate paperwork and create the sample receipt folder.

2) The package containing the sample(s) is opened, and any supporting documentation (such as a shipping manifest) is removed and retained in a sample receipt folder to be kept by the sample custodian. The contents are then inspected for any visible damage that may have occurred in transit. If this cannot be done upon receipt, the required storage condition shall be determined, and the samples will be stored accordingly. If damage is found, it will be documented on the receipt form for the sample(s). The damage will be brought to the attention of the Project Leader, who will notify the client. The appropriate course of action will be determined and taken under the supervision of the Project Leader. All actions will be documented on the Sample Receipt Form or its equivalent.

3) The Sample Receipt Form (or its equivalent) is filled out and mounted in a sample receipt notebook. A copy of this form will also be placed in the sample receipt folder. The file will be labeled with the project number and sample receipt date.

4) A unique RTI ID number is assigned to each sample by the sample custodian. Sample IDs will be assigned at the time of receipt. The RTI ID number should ensure both uniqueness and ease of tracking at a later time.

5) If required by the client, notification of sample receipt will be provided. A copy of this notification should be stored with sample receipt documentation.

4.3 Sample Custody, Tracking and Security

1) The Sample Custody Form (or its equivalent) provides custody and tracking documentation for each sample or batch of samples. The Sample Custody and Tracking form (See Attachment 2: for example) is filled out, signed, and dated by the chemist as each task is completed. Any unusual events will be noted in the “Comments” section of the form. An unusual event which compromises the sample integrity will be brought to the attention of the Project Leader for action and documentation. Samples will be considered secure, if at a minimum, the laboratory section of the building is locked with only authorized personnel having access.

2) Prior to reporting results to the client, sample information noted in the analytical report will be compared to any sample custody form or information to ensure that each sample received has the requested analytes reported or, if not, that an explanation is included in the report. This custody form (or copies, as determined by the Project Leader) will be included in the study file

at the conclusion of the study.

Documentation of sample custody and tracking operations may also be combined with sample receipt on one form (See Attachment 3: for example).

4.4 Sample Storage

1) Samples will be stored in an appropriate locked/secured location for the sample matrix (i.e., freezer, refrigerator, or sample custody room). The samples will reside in an appropriate secondary container such that the samples will be kept together and segregated from other samples. The label on this container should contain the following information:

- Date received
- Project / Task number
- Sample custodian
- Relevant notebook references
- Storage location
- Disposal date (if known)

2) Samples will be stored during the study at the location indicated on the Sample Receipt Form (or its equivalent). The location of the archived samples will also be indicated on the Sample Custody and Tracking Form (or equivalent).

4.5 Sample Disposal

1) Once samples have reached the disposal date, one of three things can happen, as dictated by the client. If the client doesn't indicate a preference, the samples will be disposed as follows.
   a) Solids and hazardous samples can be incinerated.
   b) Digested samples can go into an acid waste collector.
   c) Samples can be shipped back to the client.

2) Once samples are discarded or returned to the client, the appropriate sections of the sample custody and tracking form(s) will be filled out. Forms (or form copies) will be placed in the sample receipt folder for storage with the completed project.

Attachment 1: Sample Receipt Form

RTI Sample Receipt Form

Sample Custodian: _____

RTI Project / Task Number: _____

Client Study No. : _____

Client Sample ID(s): _____

Date Received: _____

RTI ID No(s): _____

Number of Samples: _____

Description: _____

Sample Storage Location: _____

RTI Study Code/RTI Protocol Number (if applicable): _____

Comments (hazards, etc.): _____

_____

Sample Receipt Inspection Checklist:

____ All samples were received in good condition.

____ The following discrepancies were found (see attached sheet if necessary):

____ The following actions were taken to resolve discrepancies (see next page if necessary):

Sample IDs (see next page if necessary, or attach client-provided spreadsheet with RTI IDs that have been added by RTI sample custodian):

Client ID	RTI ID	Client ID	RTI ID	Client ID	RTI ID	Client ID	RTI ID

Acknowledgment of Receipt	
Sample Custodian	**Date**

Attachment 2: Sample Custody and Tracking Form

Sample Custody and Tracking Form

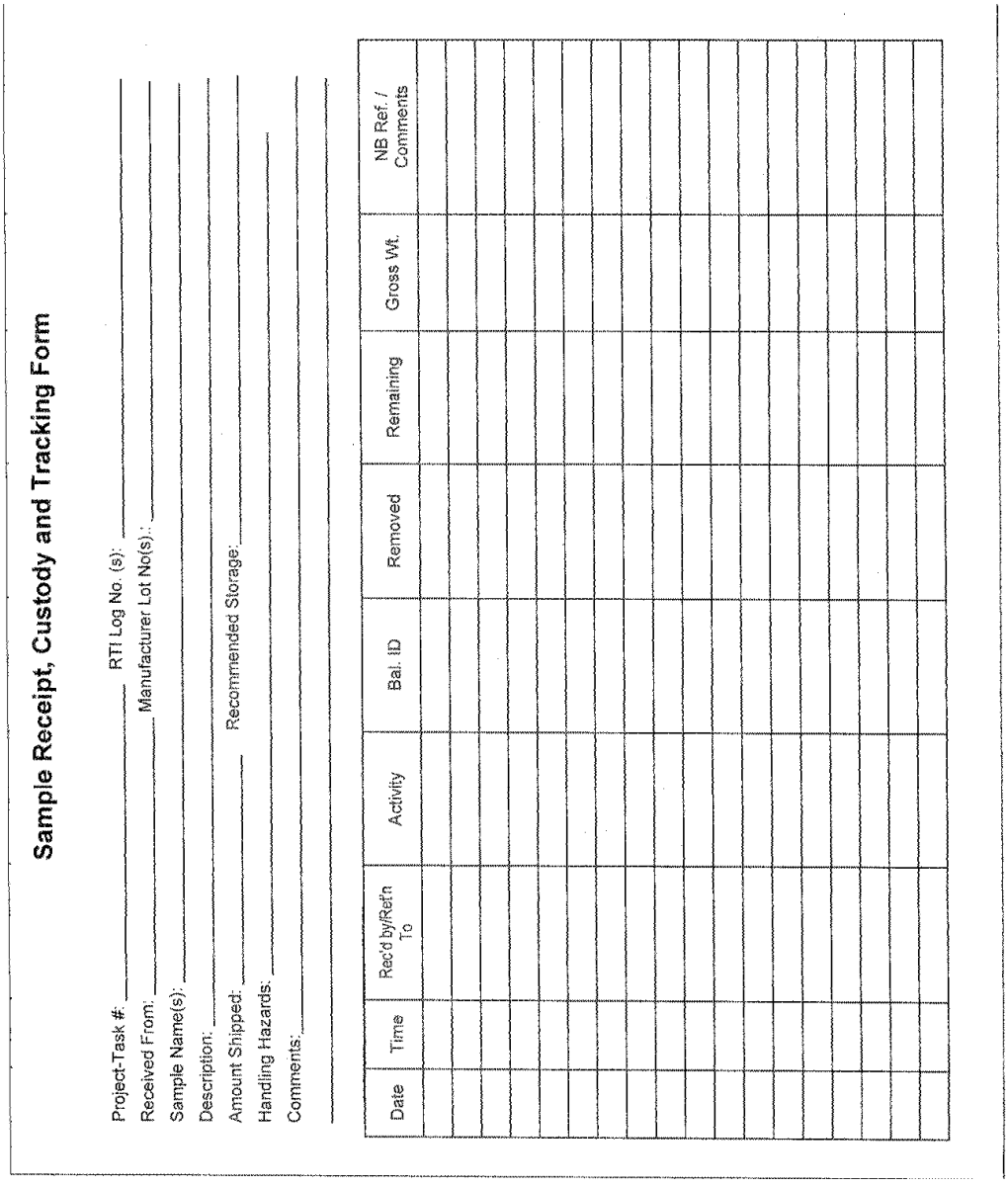
RTI/ID	Client ID	Location	Chemist / Time-Date In	Chemist/ Time-Date Out	Comments

Archived sample(s) location: _____

Date sample(s) shipped back / disposed of (circle one): _____

Sample(s) shipped back / disposed of (circle one) by: _____

Attachment 3: Sample Receipt, Custody and Tracking Form



Sample Receipt, Custody and Tracking Form

Project-Task #: _____ RTI Log No. (s): _____

Received From: _____ Manufacturer Lot No(s): _____

Sample Name(s): _____

Description: _____ Recommended Storage: _____

Amount Shipped: _____

Handling Hazards: _____

Comments: _____

Date	Time	Rec'd by/Refn To	Activity	Bal. ID	Removed	Remaining	Gross Wt.	NB Ref. / Comments

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SOP Number:	TID-LAB-005	
SOP Title:	Metals and Inorganic Analysis Sample Receipt, Storage and Tracking	

REVIEW & REVISION HISTORY

Version	Describe Major Changes or Indicate "Reviewed with No Revisions"	Effective Date/ Review Date	New Review Date
0	Replaces SOP ESE-102 and ACS-170-020	02/15/2005	02/2007
1	Updated SOP to reflect current procedures	05/03/2005	05/2007
1	SOP has been reviewed, no revision required.	05/03/2005 05/15/2007	05/2009
1	SOP has been reviewed, no revision required.	05/03/2005 3/4/2009	3/4/2012

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Appendix 5

ESE 300, Internal Quality Audits, 3 pages

TITLE: **INTERNAL QUALITY AUDITS**

AUTHOR: Signed _____
Deborah L. Franke
CEET Representative to ESE Quality Council

Date _____

APPROVED BY: Signed _____
Malcolm J. Bertoni
ESE Quality Manager

Date _____

Signed _____
Dennis F. Naugle
ESE Research Vice President

Date _____

EFFECTIVE DATE: September 1, 2000

REVISION HISTORY

REVISION NUMBER	SUMMARY OF REVISION	EFFECTIVE DATE OF REVISION
0	Original issue.	September 1, 2000

Internal Quality Audits

Purpose: This Standard Operating Procedure (SOP) is one of a series enabling ESE to document its procedures for day-to-day operational use and for training of new employees. It is intended that this SOP be compliant to all issues in ESE Quality Manual 2.9; ANSI/ASQC E4 Part A, 2.9 and ISO-9001, Paragraph 4.17.

Scope: This SOP describes the ESE system of internal quality audits done under the aegis of ANSI/ASQC E4. It is intended to also provide for ISO-9001 compliant audits in the future. ANSI/ASQC E4 recognizes two types of internal audits or assessment: management and technical. ESE SOP 420, Technical Assessment, provides more information.

Procedure:

For an ESE audit, the ESE Quality Manager or their designee shall be the responsible party. For a project audit, the project Quality Manager or Quality Assurance Officer or their designee shall be the responsible party. Checklists for performing specific types of audits are available; see the ESE Quality Council for further information.

Additional procedures for the audits will be developed by the responsible parties as necessary. These procedures shall include, at a minimum,

1. Specification of qualifications for personnel conducting each type of assessment,
2. Provision for planning, scheduling, conducting, documenting, evaluating, and reporting the results of assessments,
3. Statement to ensure that assessments include an evaluation to determine and verify whether technical requirements are being implemented correctly
4. Provision for review and authorization for timely response, based on the results of the assessments,
5. Provision for specification, implementation, and documentation of follow-up actions.

The responsible party shall have sufficient authority and organization freedom to:

1. Identify and document problems that affect quality.
2. Identify and cite noteworthy practices that may be shared with others to improve the quality of their operations and products.
3. Propose recommendations (if requested) for resolving problems that affect quality.
4. Independently confirm implementation and effectiveness of solutions.
5. Provide documentation assurance (if requested) to line management that, when problems are identified, further work performed is monitored carefully until the problems are suitably resolved.

Assessments results shall be documented, reported to and reviewed by management. Results shall be considered Quality Records and controlled according to ESE SOP 290, Control of Quality Records.

When recommendations are made, they should be handled in a timely manner, according to ESE SOP 400, Quality Improvement.

Related Procedures and References:

1. ANSI/ASQC E4-1994, *Specifications and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Program.* Available from American Society for Quality Control, Milwaukee, WI.
2. ISO-9001, ANSI/ASQC *Q9001, Quality Systems—Model for Quality Assurance in Designing, Development, Protection, Installing and Servicing.* Available from American Society for Quality Control, Milwaukee, WI.
3. ESE, *Quality Manual.* Available on the RTI Intranet.
4. ESE, *Standard Operating Procedures*, Available on the RTI Intranet.
   ESE SOP 290, *Control of Quality Records*,
   ESE SOP 400, *Quality Improvement*,
   ESE SOP 420, *Technical Assessment*.

Appendix 6

EISD 420, Technical Assessments, 5 pages

EISD
STANDARD OPERATING PROCEDURE
SOP No. 420

TITLE: Technical Assessments

SOURCE: Environmental & Industrial Sciences Division
RTI International
3040 Cornwallis Rd
Research Triangle Park, NC 27709

AUTHOR: Signed: James B. Flaherty
Date: 12/21/2010

REVIEWED BY: Signed: Cynthia A. Salmons
Date: 12/21/10

APPROVED BY: Signed: Barbara Hazen
Date: 12/21/10

Technical Assessments

Purpose:

This procedure documents the planning, implementation, and documentation of technical assessments of environmental data operations.

Scope:

This procedure applies to DAS technical self-assessments and independent technical assessments of environmental data collection programs and environmental technology programs conducted within DAS/EISD or by contractors and subcontractors performing work on behalf of DAS/EISD.

Technical assessments are conducted as part of a project's or program's quality system. These assessments are based on objective criteria provided by contract requirements, applicable standards, such as ISO-9001, and by the project's planning and quality assurance documentation including quality assurance project plans (QAPPs) and quality management plans (QMPs). DAS SOP 300, Internal Quality Audits, discusses both technical and management assessments.

Responsibility:

1. For self assessments, a designated lead auditor is responsible for the conduct of the assessment and for coordinating and overseeing other assessment team members. The lead auditor is responsible for communications with the auditee and for reporting the results of the assessment.
2. All members of the self assessment team are responsible for conducting assessment in a systematic, objective and professional manner. They are responsible for communicating assessment findings to the lead auditor.
3. For all assessments, the manager of the project or program being assessed is responsible for preparing planning documents, such as QAPPs and QMPs, that clearly describe data quality objectives and/or data quality indicators for the project or program. This individual is responsible for implementing the environmental data operation in accordance with these documents and for implementing corrective action in response to assessment findings.
4. Project or program personnel are responsible for cooperating with the assessment team members for all assessments.

Procedures:

1. Auditors should have a minimum of four years' full-time appropriate practical workplace experience (not including training), at least two years of which should have been in quality assurance activities.
2. Auditors should have undergone training to the extent necessary to ensure their competence in the skills required for conducting and managing audits.

3. Auditors assigned to conduct a specific audit should collectively possess adequate professional proficiency for the tasks required.
4. Auditors should be free from personal and external barriers to independence, be organizationally independent, and be able to maintain an independent attitude and appearance.
5. Auditors should use due professional care in conducting the audit and in preparing related reports.
6. Auditors should be supervised and evaluated to ensure high-quality and professional work. Audit program management should be carried out by personnel with a practical knowledge of technical audit procedures and practices. Audit program management should be independent of direct responsibility for implementing the projects being assessed.
7. The authority and independence of auditors, and the limits on their authority, must be clearly defined in planning documents, such as QAPPs and/or QMPs for the project or program being assessed.
8. The lead auditor and the assessment team will develop a written audit plan that addresses the project or program to be assessed, the tentative date and place of the assessment, the scope and purpose of the assessment, objective assessment criteria (which may be part of an audit questionnaire or audit checklist), and the confidentiality and dissemination of assessment findings.
9. In most cases, the technical assessment will be based on objective assessment criteria derived from the QAPP and/or the QMP, although other planning documentation also may be used.
10. A graded approach will be used in planning and implementing the assessment.
11. An assessment will begin and end with a meeting between the assessment team and the management and key personnel of the project or program being assessed. The meetings will be led by the lead auditor. The assessment agenda, the scope and the purpose of the assessment, and the objective assessment criteria will be discussed in the opening meeting. Audit findings (i.e., noteworthy practices, observations and nonconformances) and the objective evidence for these findings are the subject of the closing meeting.
12. The assessment team will use the following assessment techniques: observing work in progress; interviews, document review; and objective evidence compilation.
13. The lead auditor will be responsible for preparing a draft findings report (DFR) and for organizing work to get the report written. The DFR should summarize the assessment findings and, if appropriate, it may include conclusions, recommendations, and suggested corrective action. The DFR should be prepared within approximately 30 days of the completion of the assessment. The DFR should be sent to the auditee and program management for review and comment.
14. The lead auditor will prepare a final report based on the DFR and any comments about the DFR.
15. There must be clear authority in planning documents, such as QAPPs and/or QMPs, for implementing any corrective actions to be taken in response to assessment findings.
16. The management of the project or program being assessed will plan and implement corrective action in response to assessment findings and it will determine the effectiveness of the corrective action. Corrective action in response to assessment findings will be documented and this documentation will be sent to the lead auditor.
17. The lead auditor will prepare documentation of the formal closeout of the assessment after corrective actions have been implemented and confirmed as effective.

Documentation and Records Management:

Assessment planning documents, assessment questionnaires and checklists, assessment findings reports, and documentation of corrective action are quality records and they are to be managed and stored in accordance with RTI/DAS quality system policies, including considerations of records retention, security and confidentiality. Assessment-related documents generated as part of a contractually required internal audit program will be retained as required by the contract, or for a minimum of 5 years.

Related Procedures and References:

1. ANSI/ASQC E4-1994, *Specifications and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Program.* Available from America Society for Quality Control, Milwaukee, WI.
2. ISO-9001, ANSI/ ASQC Q9001, *Quality Systems - Model for Quality Assurance in Designing, Development, Protection, Installing and Servicing*. Available from American Society for Quality Control, Milwaukee, WI.
3. DAS, *Quality Manual.* Available on the RTI intranet.
4. DAS SOP 300, *Internal Quality Audits,* available on the RTI Intranet
5. Russell, P.P. (editor). 1977. *The Quality Audit Handbook*. ASQ Quality Press. Milwaukee, Wisconsin.
6. U.S. Environmental Protection Agency. 2000. *Guidance on Technical Audits and Related Assessments for Environmental Data Operations, EPA QA/G-7*, publication EPA/600/R-99/080.

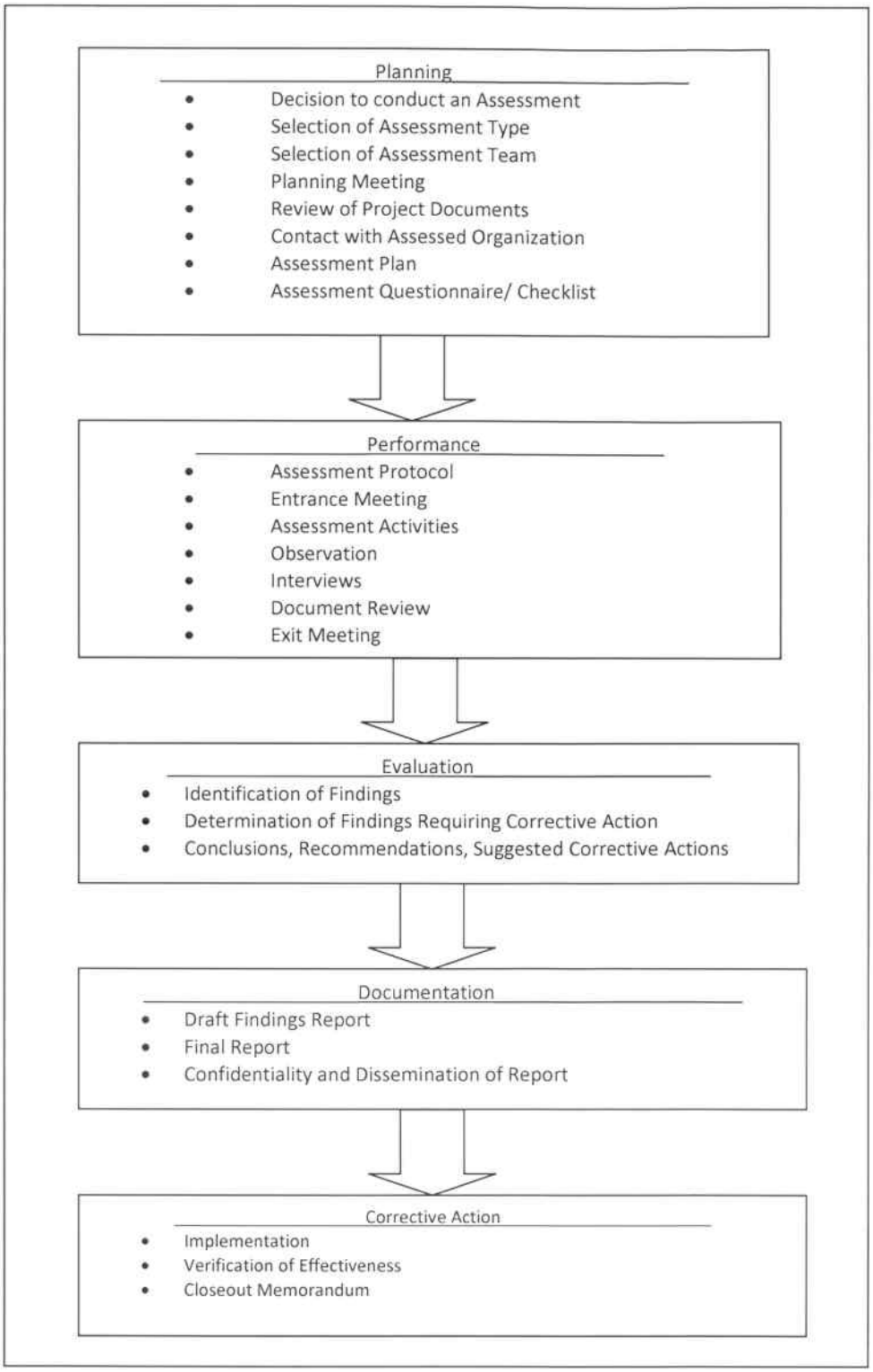

Figure 1. A generalized flowchart of a technical assessment.